1983

Chemistry of 2,3-dimethylene-2,3-dihydrofurans and other reactive olefins prepared by the flash vacuum pyrolysis of substituted furylmethyl esters

Timothy John Cassady
Iowa State University

Recommended Citation

Cassady, Timothy John, "Chemistry of 2,3-dimethylene-2,3-dihydrofurans and other reactive olefins prepared by the flash vacuum pyrolysis of substituted furylmethyl esters " (1983). *Retrospective Theses and Dissertations*. 8459.
https://lib.dr.iastate.edu/rtd/8459

INFORMATION TO USERS

This reproduction was made from a copy of a document sent to us for microfilming. While the most advanced technology has been used to photograph and reproduce this document, the quality of the reproduction is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help clarify markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure complete continuity.
2. When an image on the film is obliterated with a round black mark, it is an indication of either blurred copy because of movement during exposure, duplicate copy, or copyrighted materials that should not have been filmed. For blurred pages, a good image of the page can be found in the adjacent frame. If copyrighted materials were deleted, a target note will appear listing the pages in the adjacent frame.
3. When a map, drawing or chart, etc., is part of the material being photographed, a definite method of "sectioning" the material has been followed. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.
4. For illustrations that cannot be satisfactorily reproduced by xerographic means, photographic prints can be purchased at additional cost and inserted into your xerographic copy. These prints are available upon request from the Dissertations Customer Services Department.
5. Some pages in any document may have indistinct print. In all cases the best available copy has been filmed.

University
Microfilms
International

300 N. Zeeb Road
Ann Arbor, MI 48106

Cassady, Timothy John

CHEMISTRY OF 2,3-DIMETHYLENE-2,3-DIHYDROFURANS AND OTHER REACTIVE OLEFINS PREPARED BY THE FLASH VACUUM PYROLYSIS OF SUBSTITUTED FURYLMETHYL ESTERS

Iowa State University PH.D. 1983

University
Microfilms
International 300 N. Zeeb Road, Ann Arbor, MI 48106

Chemistry of 2,3-dimethylene-2,3-dihydrofurans and other reactive olefins prepared by the flash vacuum pyrolysis of substituted furylmethyl esters

by

Timothy John Cassady

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1983

TABLE OF CONTENTS

LIST OF FIGURES

Page

For General Introduction:

For Section I:

Page

For Section III:

For Section V:

For Section VI:

LIST OF TABLES

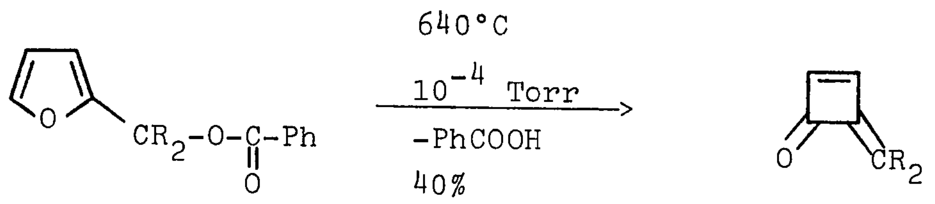
For Section III:

For Section IV:

For Section VI:

GENERAL INTRODUCTION

The flash vacuum pyrolysis (FVP) of furfuryl benzoate (1a) was reported several years ago to give a moderate yield of 4-methylenecyclobut-2-enone (2a), along with benzoic acid and some minor products.[1] This unexpected transformation made available the parent compound of a series of compounds which is not easily synthesized.[2] Prior to that report, 4-methylenecyclobut-2-enone (2a) was one of the unknown cyclobutadiene derivatives[3] and is a potentially useful, synthetic intermediate since it has a highly functionalized cyclobutane ring.



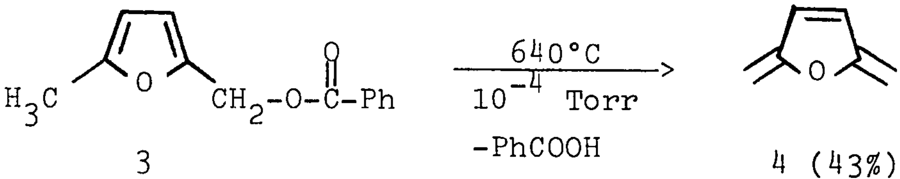
1a, R=H

1b, R=D

2a, R=H

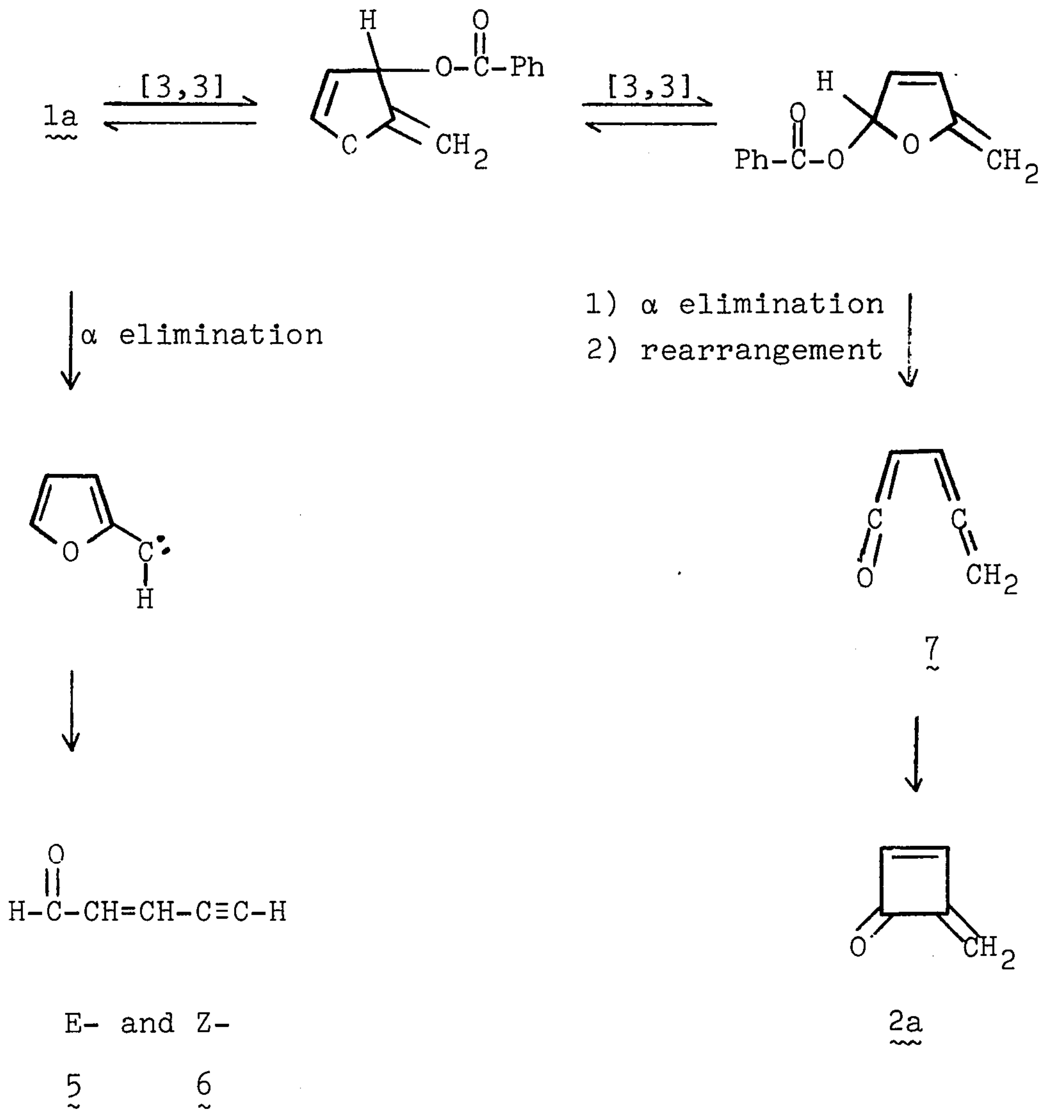
2b, R=D

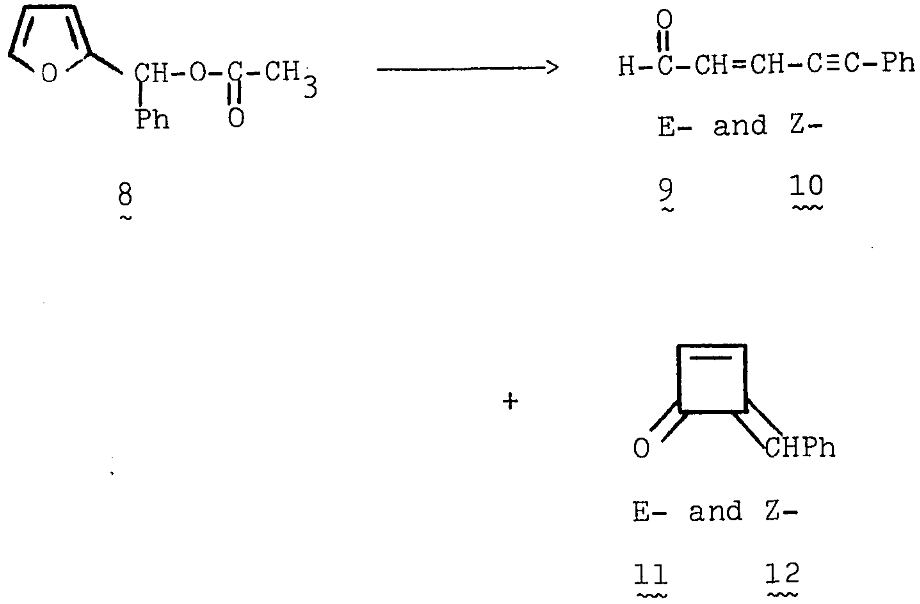
In order to determine the scope of the reaction and to achieve a better understanding of its mechanism, a study of the pyrolysis chemistry of a series of substituted furfuryl esters was undertaken. A mechanism for the conversion of **1a** to **2a** was proposed on the basis of a deuterium-labeling experiment, **1b** to **2b**, and on a study of the pyrolysis products formed from 5-methylfurfuryl benzoate (**3**).[4]



3 **4** (43%)

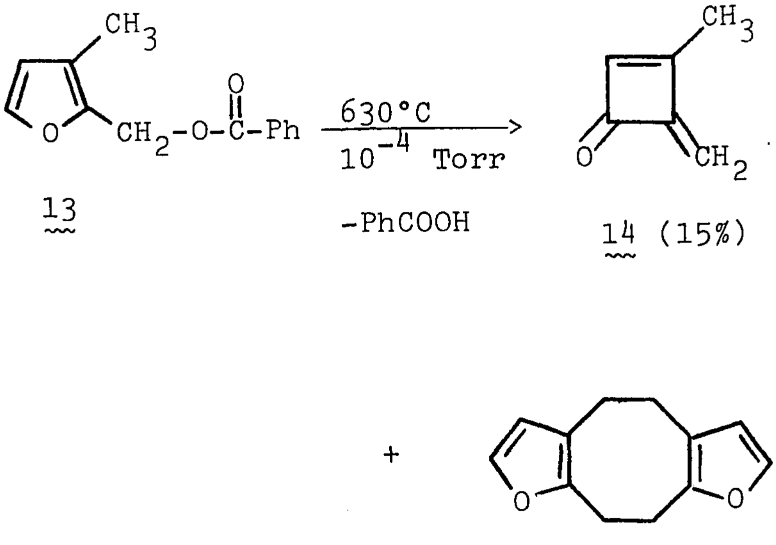
The proposed mechanism for the formation of the pyrolysis products from **1** involved α eliminations of benzoic acid after zero to two [3,3] sigmatropic shifts of the benzoate group around the furan ring. Support for this mechanism was obtained from a study of the pyrolysis products formed from α-phenylfurfuryl acetate (**8**). Experiments involving samples of **8** which were labeled with deuterium on the α carbon were run in order to obtain experimental evidence for the proposed mechanisms for the formation of the pyrolysis products from **8**.


1a
[3,3]
H
O-C-Ph
CH2
[3,3]
H
Ph-C-O
O
CH2
α elimination
1) α elimination
2) rearrangement
O
C
H
C
O
C
CH2
7
H-C-CH=CH-C≡C-H
E- and Z-
5
6
O
CH2
2a



Further support for the migration mechanism came from a preliminary study of the pyrolysis products formed from 3-methylfurfuryl benzoate (13). Pyrolysis of 13 at 640°C and 10^{-4} Torr formed as major products 3-methyl-4-methylenecyclobut-2-enone (14) and the head-to-head, [4+4] dimer 15 of 2,3-bis(methylene)-2,3-dihydrofuran (16).[6]

Initially, there were several goals to this project. The first goal was to determine if the formation of [4+4] dimer 15 occurred via the intermediacy of 2,3-dimethylene-2,3-dihydrofuran (16). The pyrolysis chemistry of a series of methyl-substituted, furfuryl esters was studied over a wide range of pyrolysis temperatures in order to provide

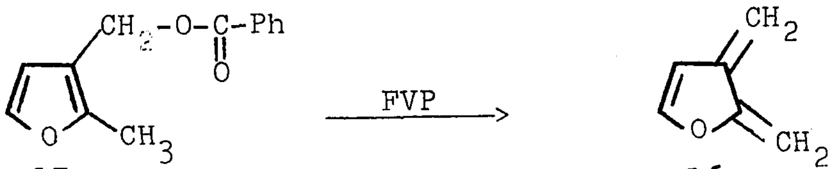


13

14 (15%)

15 (20%)

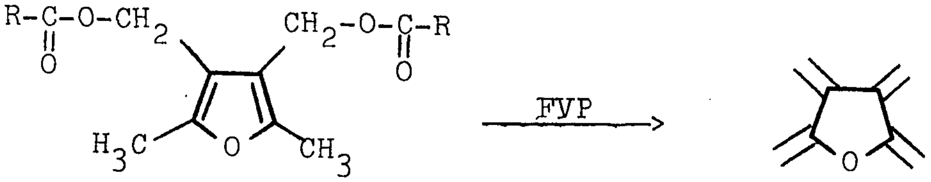
further experimental evidence for the migration mechanism proposed for the conversion of 1 to 2. A consideration of this mechanism suggested that the pyrolysis of 2-methyl-3-furylmethyl benzoate (17) would generate 16 in the absence of 14. A study of the pyrolysis chemistry of several substituted 2-methyl-3-furylmethyl benzoates was undertaken in order to study the chemistry of the resulting 2,3-dimethylene-2,3-dihydrofurans. The Diels-Alder reactions of these reactive intermediates were studied, in addition to their chelatropic reactions with sulfur dioxide and their dimerization reactions. These compounds are the furan analogs of the *ortho*-quinodimethanes, an actively-investigated group of reactive intermediates.[7-12]



17 16

A study of the pyrolysis chemistry of 3-furylmethyl benzoate (18) was initiated in order to provide additional evidence for the migration mechanism proposed for the formation of the pyrolysis products from furfuryl benzoate (1a).

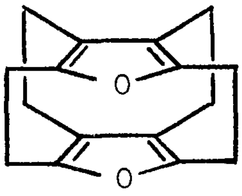
In order to test the generality of the method for producing 2,3-dimethylene-2,3-dihydrofuran (16) by the pyrolysis of 2-methyl-3-furylmethyl benzoate (17), a synthesis of furanoradialene (19) was undertaken. The



20 19

pyrolysis chemistry of diesters 20 of 3,4-bis(hydroxymethyl)-2,5-dimethylfuran was studied as a means of obtaining 19. The Diels-Alder reactions of 19 and the chelatropic reaction of 19 with sulfur dioxide were investigated in order to to study the chemical reactivity of 19.

The synthetic utility of the method for producing 2,3-dimethylene-2,3-dihydrofuran (16) was tested by using this method in several approaches to the synthesis of [2.2.2.2](2,3,4,5) furanophane (21).



21

Description of the pyrolysis apparatus. The pyrolysis apparatus is pictured in Figure 1. The dimensions of the components have been previously reported[13] and a commercially-available version of the apparatus is available from Kontes Scientific Glassware.

Explanation of dissertation format. This dissertation has been written using the alternate dissertation format and consists of six sections written as complete papers in a style suitable for publication in journals published by the American Chemical Society. Section I has been recently published in the Journal of the American Chemical Society.[14] All of the experimental results presented in Sections I through VI were contributed by the candidate.

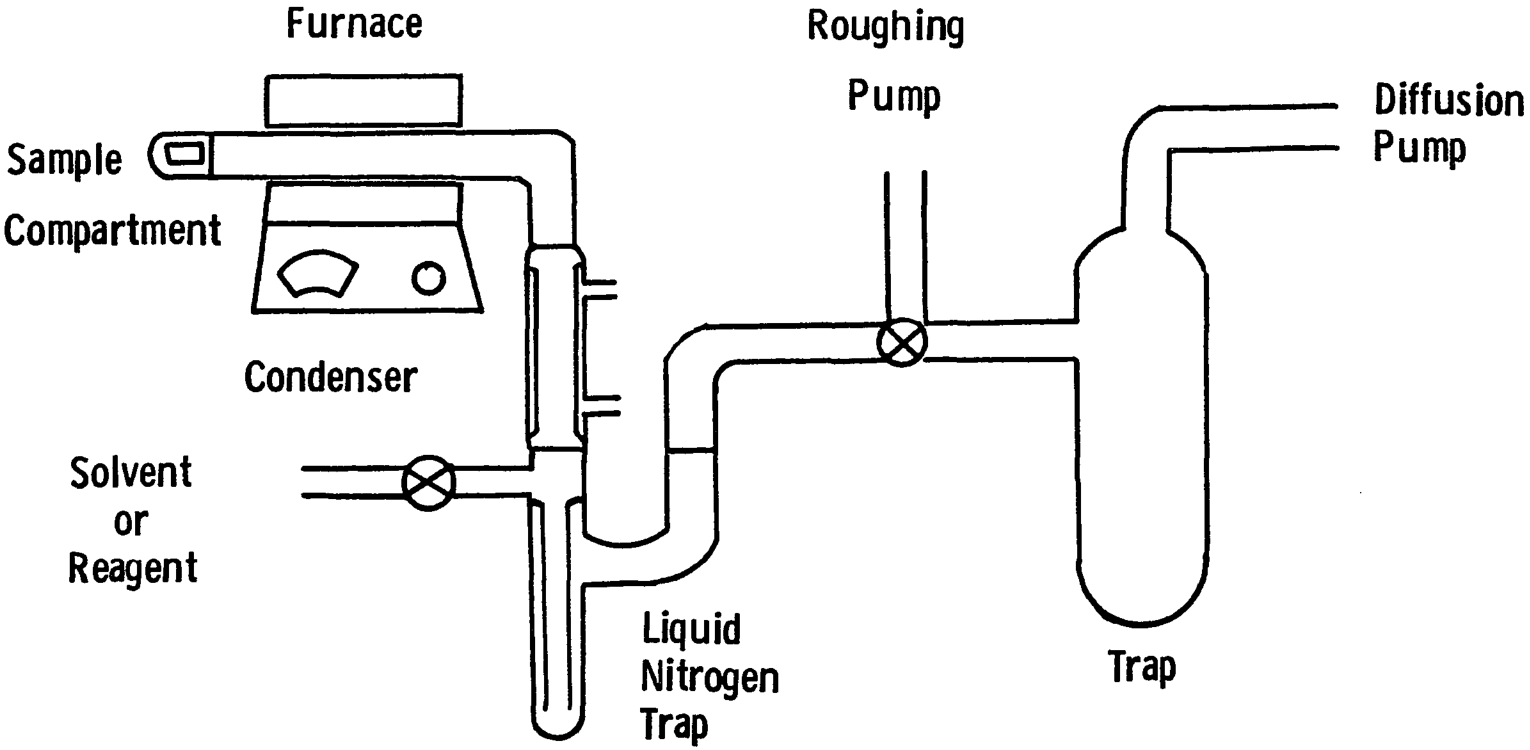
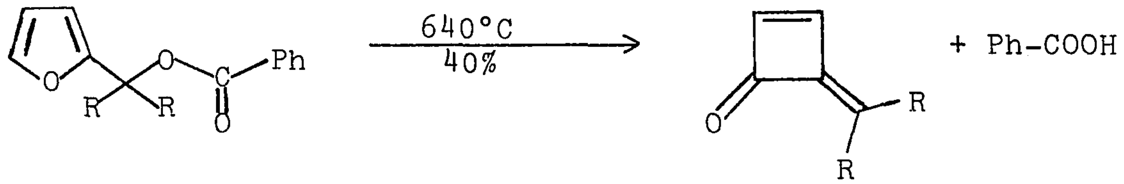


Figure 1. Diagram of the pyrolysis apparatus

SECTION I. PREPARATION OF 2,3-DIMETHYLENE-2,3-DIHYDROFURANS BY THE FLASH VACUUM PYROLYSIS OF SUBSTITUTED FURYLMETHYL ESTERS

INTRODUCTION

Several years ago we reported that the flash vacuum pyrolysis (FVP) of furfuryl benzoate (**1**a) gives a moderate yield (40%) of methylenecyclobutenone (**2**a) along with benzoic acid and some minor products.[1] In order to determine the scope of the reaction and to achieve a better understanding of its mechanism, the pyrolysis of a series of substituted furfuryl esters was undertaken.[2] A mechanism for the conversion of (**1**a) to (**2**a) was proposed on the basis of a deuterium-labeling experiment, (**1**b) to (**2**b), and on a study of the products formed from the pyrolysis of 5-methylfurfuryl benzoate (**3**).[1b]

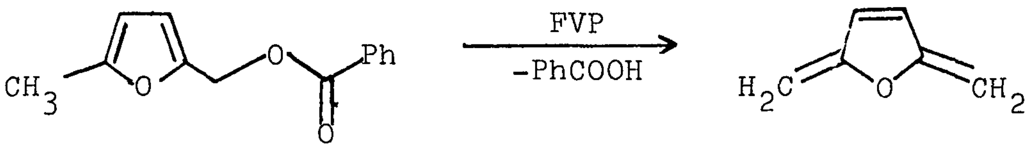


1 a R=H

b R=D

2 a R=H

b R=D



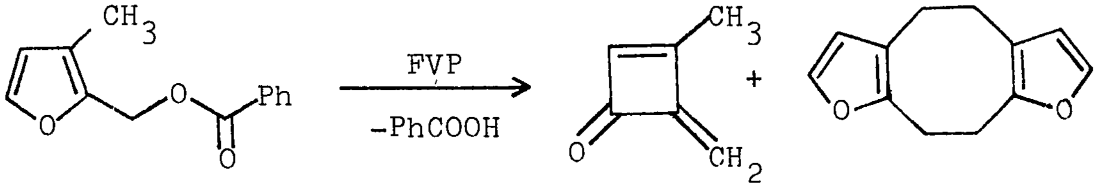
3

4 (43%)

As part of this study, the pyrolysis of 3-methylfurfuryl benzoate (**5**) was investigated because it was anticipated that pyrolysis of **5** would give 2,3-dimethylene-2,3-dihydrofuran (**6**). Compound **6** is a furan analog of the *ortho*-quinodimethanes, an extensively investigated group of reactive intermediates.[3]

RESULTS

The FVP of 5 at 620-640°C and ca. 10^{-4} Torr produced a white product band in the cold trap at 77 K. Carbon disulfide was added to the trap and the product mixture was then slowly warmed to room temperature. The major products formed were 3-methyl-4-methylenecyclobutenone (7) and 8, the head-to-head, [4+4] dimer of 2,3-dimethylene-2,3-dihydrofuran (6). These products were accompanied by the formation of benzoic acid and a substantial amount of a white polymer.



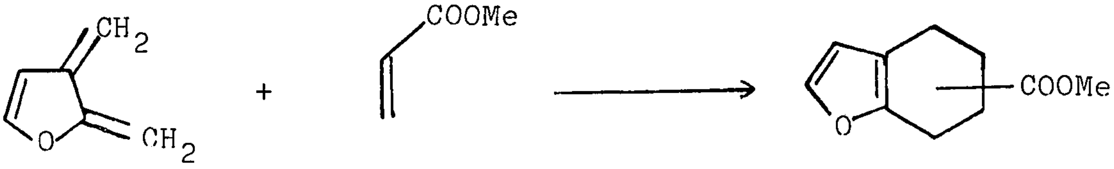
5 7 8

21% 24%

The structure of 7 was indicated by its spectral properties. The ^1H NMR spectrum included a doublet for the methyl group at δ 2.34 (J = 1.5 Hz), multiplets for the methylene hydrogens at δ 4.70 and δ 5.02, and a multiplet for the ring olefinic hydrogen at δ 6.86. The ^{13}C NMR spectrum consisted of six peaks with appropriate chemical shifts. The IR spectrum showed an intense absorption at 1779 cm^{-1} which agrees very well with the carbonyl absorption reported for 2 (1783 cm^{-1}).[1]

The structure of dimer **8** was also determined by its spectral properties. The ^1H NMR spectrum exhibited four-proton singlets at δ 2.78 and 3.04 and two-proton doublets for the furan hydrogens at δ 6.06 ($J = 2$ Hz) and 7.16 ($J = 2$ Hz). The ^{13}C NMR spectrum showed six signals, as required by the symmetry of **8**, with appropriate chemical shifts.

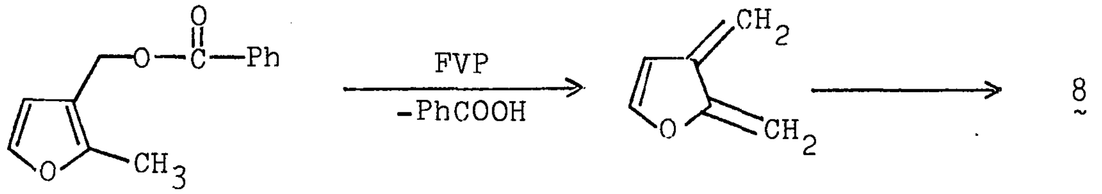
If methyl acrylate is added to a solution of the cold pyrolysis products of **5** prior to warming, a mixture of the Diels Alder adducts (**9**) is obtained along with **7** and benzoic acid. This observation indicates that **6** is the primary pyrolysis product which dimerizes to **8** upon warming.



6

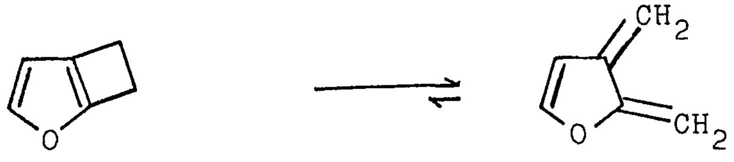
9

A consideration of the mechanism proposed for the conversion of **1** to **2** suggested that the pyrolysis of 2-methyl-3-furylmethyl benzoate (**10**) would generate **6** in the absence of **4**. The pyrolysis of **10** at 640°C and 10^{-4} Torr gave a 51% yield of dimer **8**, along with benzoic acid and a large amount of polymeric material. It was also observed that **6** could be trapped with methyl acrylate to form the same Diels-Alder adducts (**9**) that were derived from the pyrolysis products of **5**.



10 6 51%

Further proof that 6 is a primary pyrolysis product of 5 and 10 was obtained by recording the ^1H and ^{13}C NMR spectra of 6 at -60°C. The ^1H NMR spectrum of 6 can be recorded between -60°C and -100°C. At temperatures below -100°C, the solubility of 6 diminishes and dimerization occurs rapidly. The enhanced dimerization is probably caused by increased local concentrations of 6. In Figure 1, the ^1H NMR spectra of the pyrolysis products of 10, recorded at -60°C and 35°C, are presented. An interesting feature of the spectra is the absence of peaks corresponding to furanocyclobutene (11), the closed form of 6. Apparently, the resonance energy of the furan ring in 11 is insufficient to compensate for the strain energy of the four-membered ring. Thus, it appears that the open form (6) is more stable than 11.



11 6

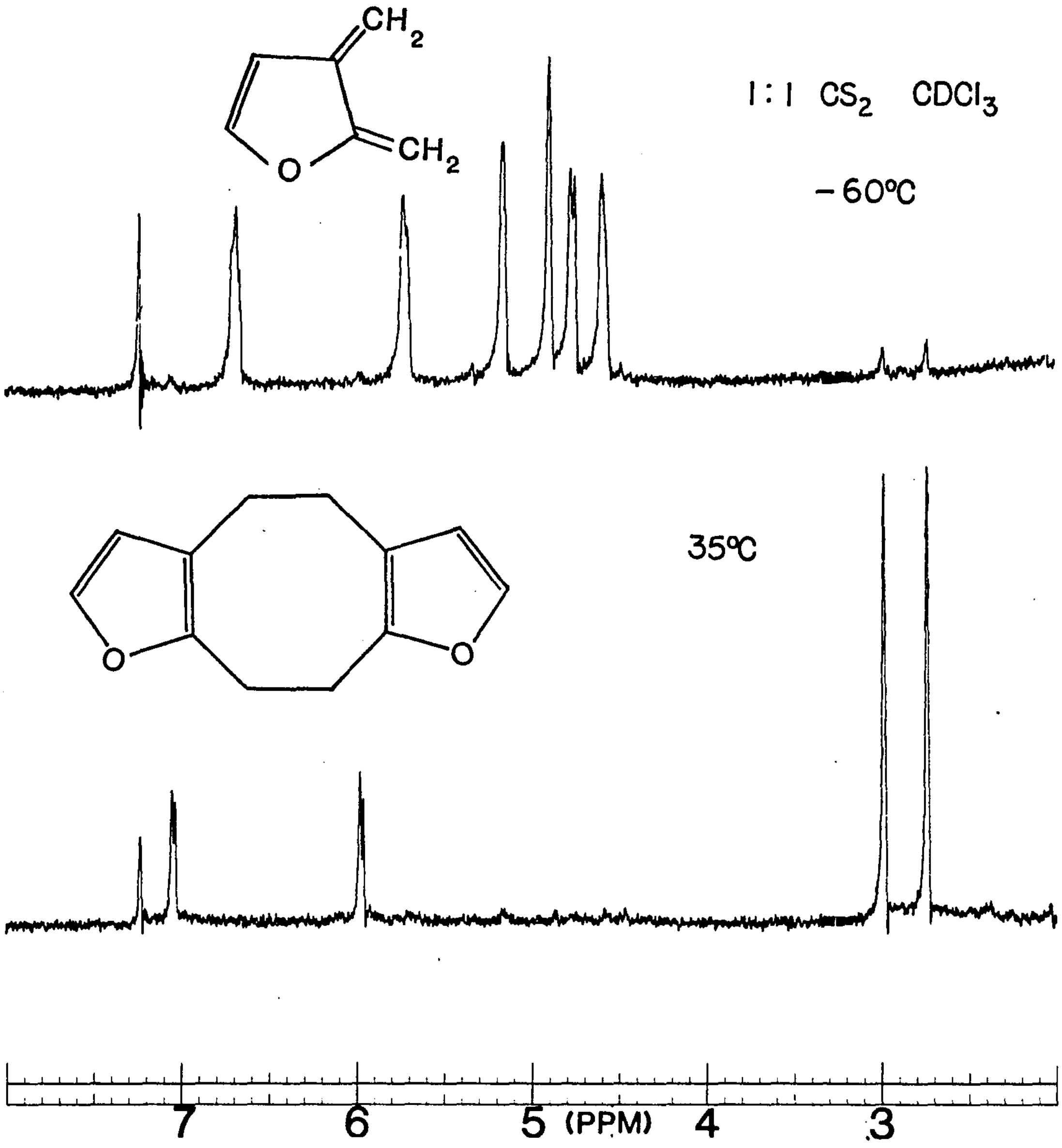
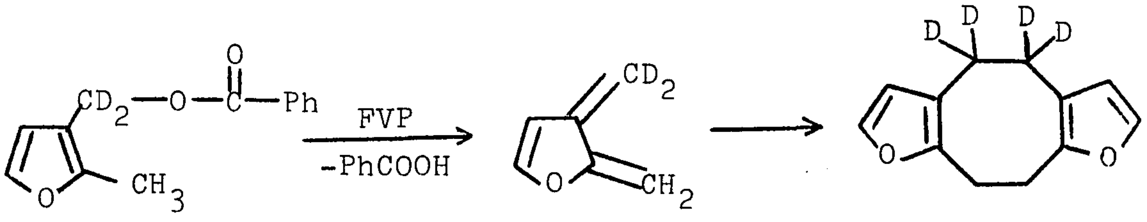


Figure 1. ^{1}H NMR spectra of the pyrolysis products formed from 2-methyl-3-furylmethyl benzoate (**10**) recorded at -60°C (top) and at 35°C (bottom) in 1:1 CS_2/$CDCl_3$ (δ 7.2 peak is due to $CHCl_3$)

The preparation and pyrolysis of **10**-d_2 was undertaken in order to assign the ^1H and ^{13}C NMR signals from **6** and **8**. A mass spectral analysis of **10**-d_2 showed greater than 95% d_2 incorporation. The ^1H and ^{13}C NMR spectra of **6**-d_2 and **8**-d_4 were recorded at -60°C and 40°C, respectively. The ^1H NMR spectrum of **6**-d_2 included a doublet at δ 6.73 (J = 1.5 Hz) and a multiplet at δ 5.78 for the ring protons and a doublet at δ 4.85 (J = 1.5 Hz) and a multiplet at δ 4.65 for the 2-methylene protons. The ^{13}C NMR spectrum of **6**-d_2 showed five peaks including one at δ 85.22 for the methylene carbon at the 2-position. A signal at δ 102 for the methylene carbon at the three position was not observed. In Figure 2, the ^1H NMR spectra of the pyrolysis products formed from **10**-d_2, recorded at -60 and 35°C, are presented.



10-d_2 **6**-d_2 **8**-d_4

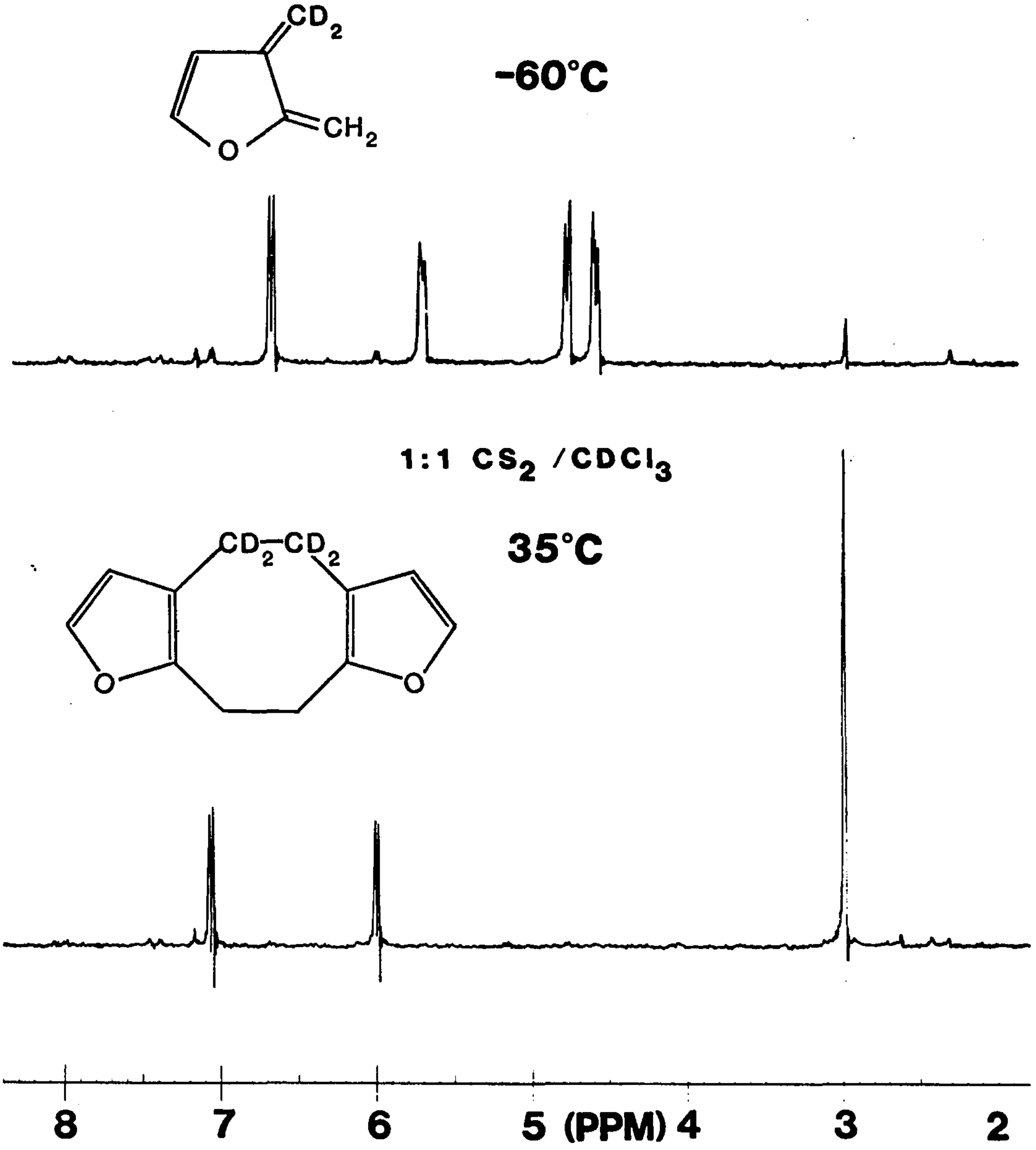
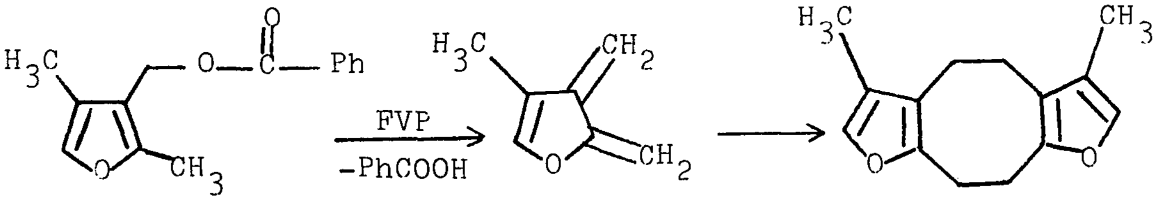


Figure 2. ^{1}H NMR spectra of the pyrolysis products formed from 2-methyl-3-furylmethyl-α,α'-$\underline{d}_2$ benzoate (10-$\underline{d}_2$) recorded at -60°C (top) and at 35°C (bottom) in 1:1 CS_2 /$CDCl_3$

The high reactivity of 6 as a diene enables its Diels-Alder reactions to serve as a direct method for obtaining the furanocyclohexane ring skeleton. Since a large number of sesquiterpenes contain a furanocyclohexane unit with a β-methyl group on the furan ring,[4] the pyrolysis of 2,4-dimethyl-3-furylmethyl benzoate (12) was investigated. The pyrolysis of 12 at 640°C and 10^{-5} Torr gave a 43% isolated yield of 13, the head-to-head, [4+4] dimer of 14, along with benzoic acid and a large amount of an off-white polymer. The structures of 13 and 14 were indicated by their ^{1}H and ^{13}C NMR spectra. In Figure 3, the ^{1}H NMR spectra of the pyrolysis products of 12 recorded at -60, -15 and 35°C, are presented.



12   14   13 (43%)

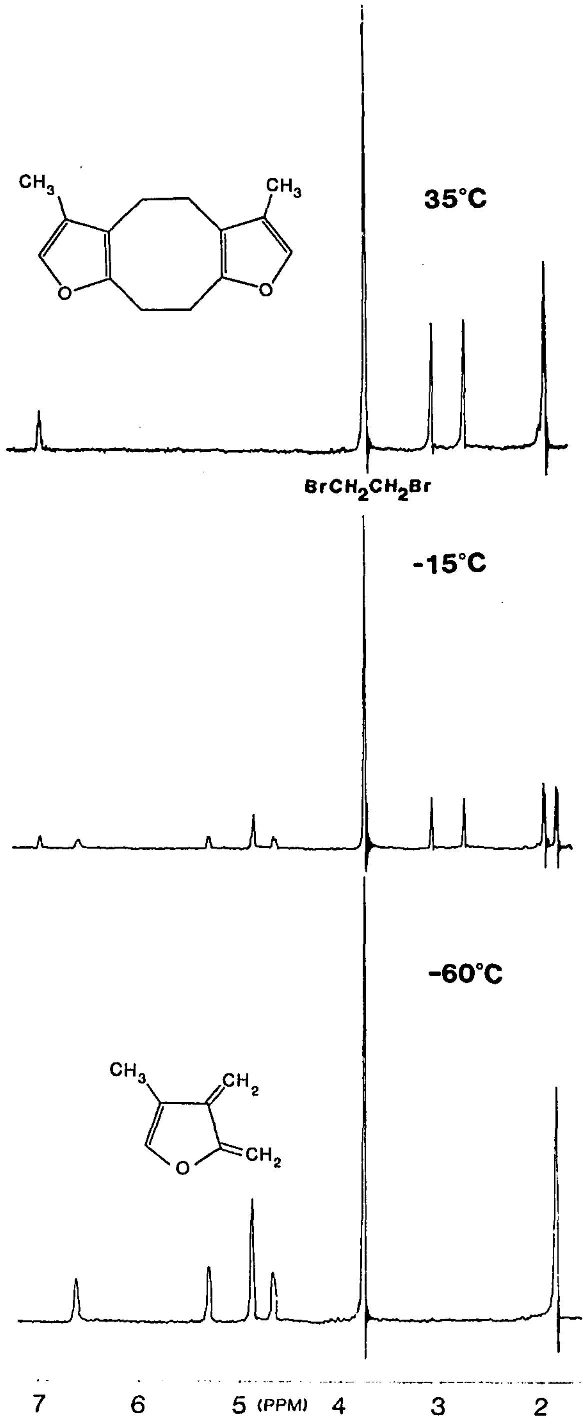
When a large excess of methyl acrylate was added to the product trap, good yields of the Diels-Alder adducts (15 and 16) were obtained (64-75%) along with small amounts of dimer (13) (2-9%) and substantial amounts of polymer.

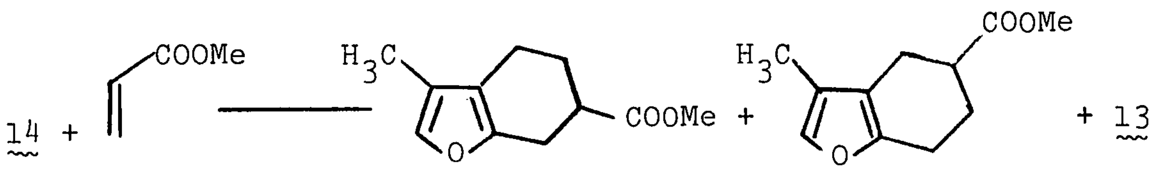
Figure 3. ^1H NMR spectra of the pyrolysis products formed from 2,4-dimethyl-3-furylmethyl benzoate (12) in CS_2 and in the presence of a dibromoethane internal standard

Top: Spectrum of [4+4] dimer 13 recorded at 35°C

Middle: Spectrum of a 2:1 mixture of 4-methyl-2,3-dimethylene-dihydrofuran (14) and [4+4] dimer 13 recorded at -15°C

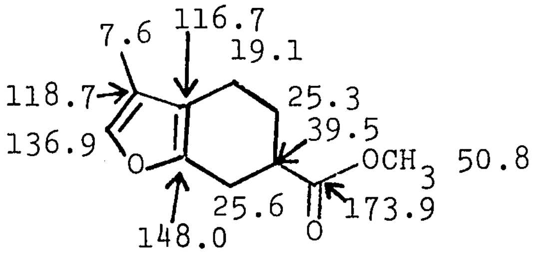
Bottom: Spectrum of 14 recorded at -60°C


CH3
CH3
35°C
BrCH2CH2Br
-15°C
-60°C
CH3
CH2
CH2
O
7
6
5 (PPM)
4
3
2

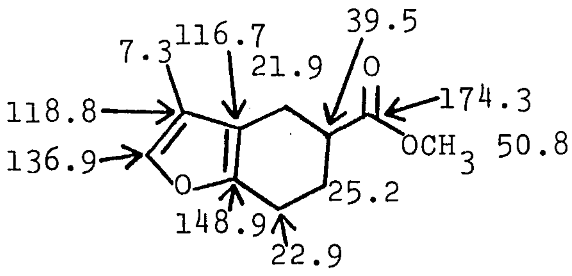


15 16

The ratio of 15 to 16 was determined by analysis of the ^{13}C NMR spectral data for mixtures of the two isomers. Five of the signals from 15 were sufficiently separated from the corresponding signals of 16 that the areas of the peaks could be used to determine the isomer ratio. An average of four determinations using this method indicated that the ratio of 15 to 16 is 3.0 to 1. The ^{13}C NMR chemical shifts ($CS_2/CDCl_3$; δ from TMS) are presented below.

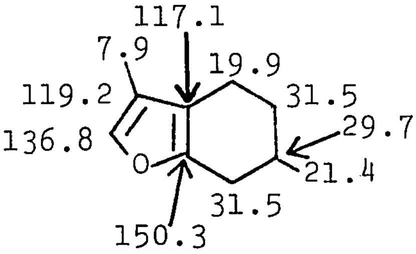


15

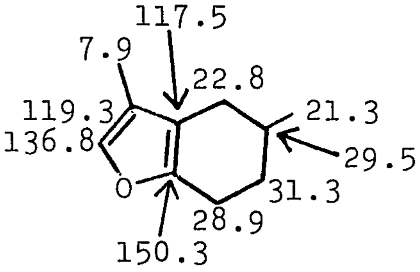


16

In order to determine the structures of 15 and 16 and to confirm the value for the isomer ratio, the carbomethoxy groups in 15 and 16 were converted to methyl groups. This converted 15 to the commercially-available, natural product methofuran (17), while 16 was converted to isomenthofuran (18). Since the IR and the ^{1}H NMR spectra of 17 and 18 were virtually superimposable except for some minor peaks in the IR spectra, it was necessary to rely on the ^{13}C NMR spectra to distinguish the isomers. The ^{13}C NMR chemical shifts ($CS_2/CDCl_3$; δ from TMS) of 17 and 18 are presented below.

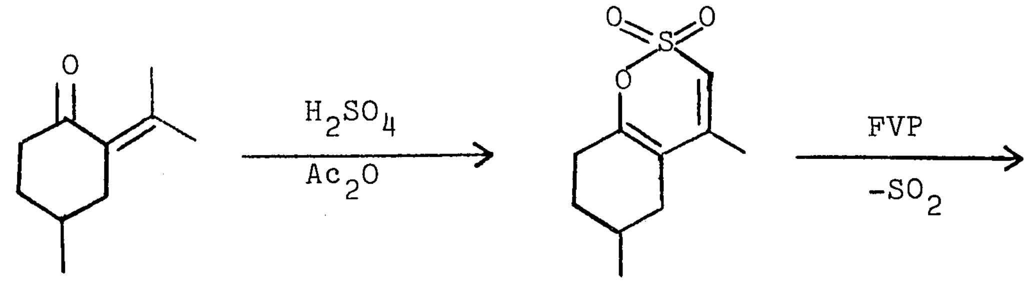


17



18

The ratio of 17 to 18 was determined to be 3.3 to 1 by comparing the areas corresponding to carbon 4 of each isomer (δ 19.9 and 22.8). Isomenthofuran (18) was synthesized by an independent route for spectral comparison. 2-Isopropylidine-4-methylcyclohexanone (19)[5] was converted to the δ-sultone (20) by treatment with sulfuric acid in acetic anhydride.[6] The δ-sultone was then pyrolyzed at 640°C and 10^{-4} Torr to eliminate sulfur dioxide and form 18. The ^{1}H NMR and IR spectra of 17, 18 and a mixture of 17 and 18 are presented in Figures 4 and 5 respectively.



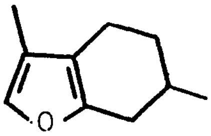
18

75%

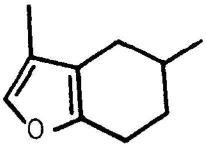
19

20 (36%)

Figure 4. ^{1}H NMR spectra of isomethofuran (18) (top), a 3:1 mixture of menthofuran (17) and isomenthofuran (18) (middle), and menthofuran (17) (bottom) in CS_2 at 35°C



17



18

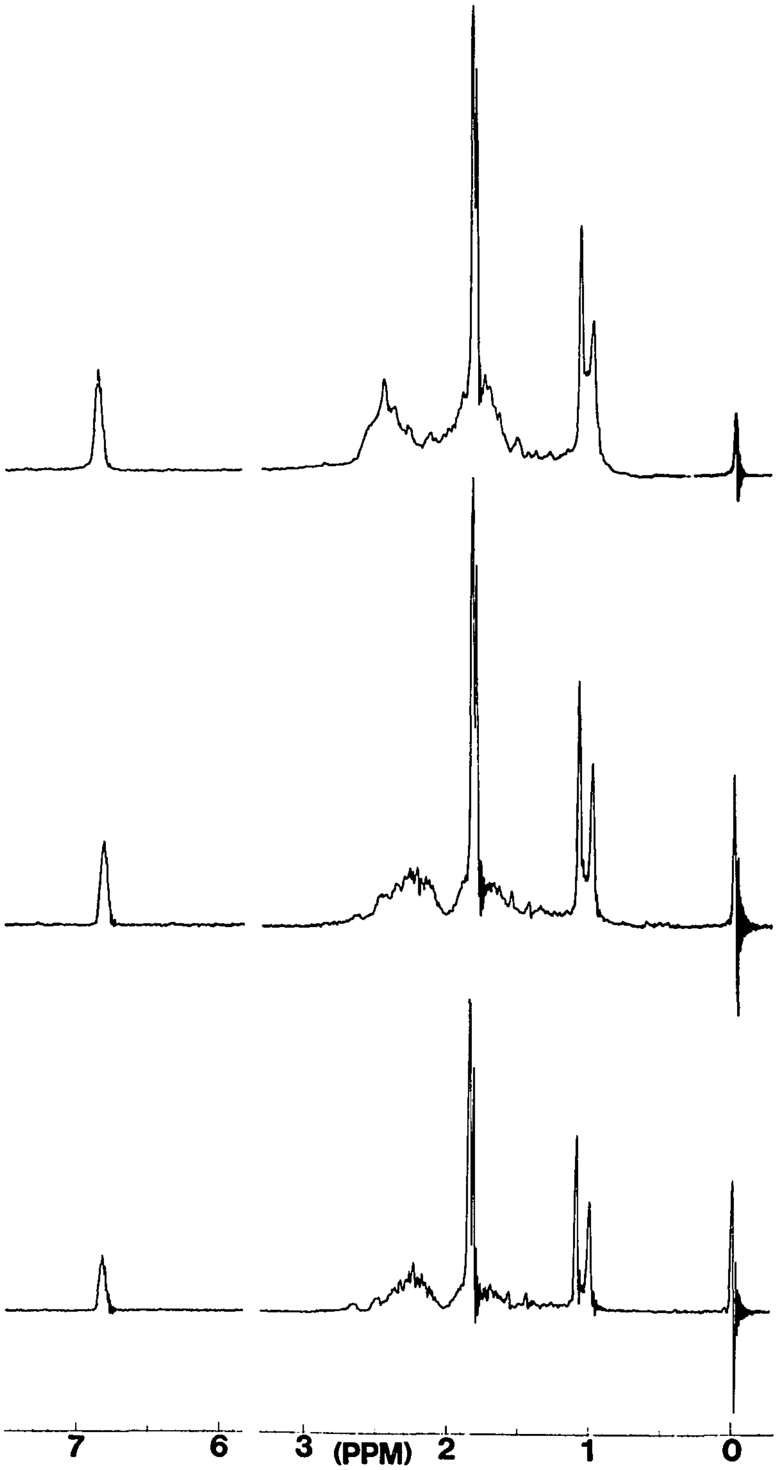
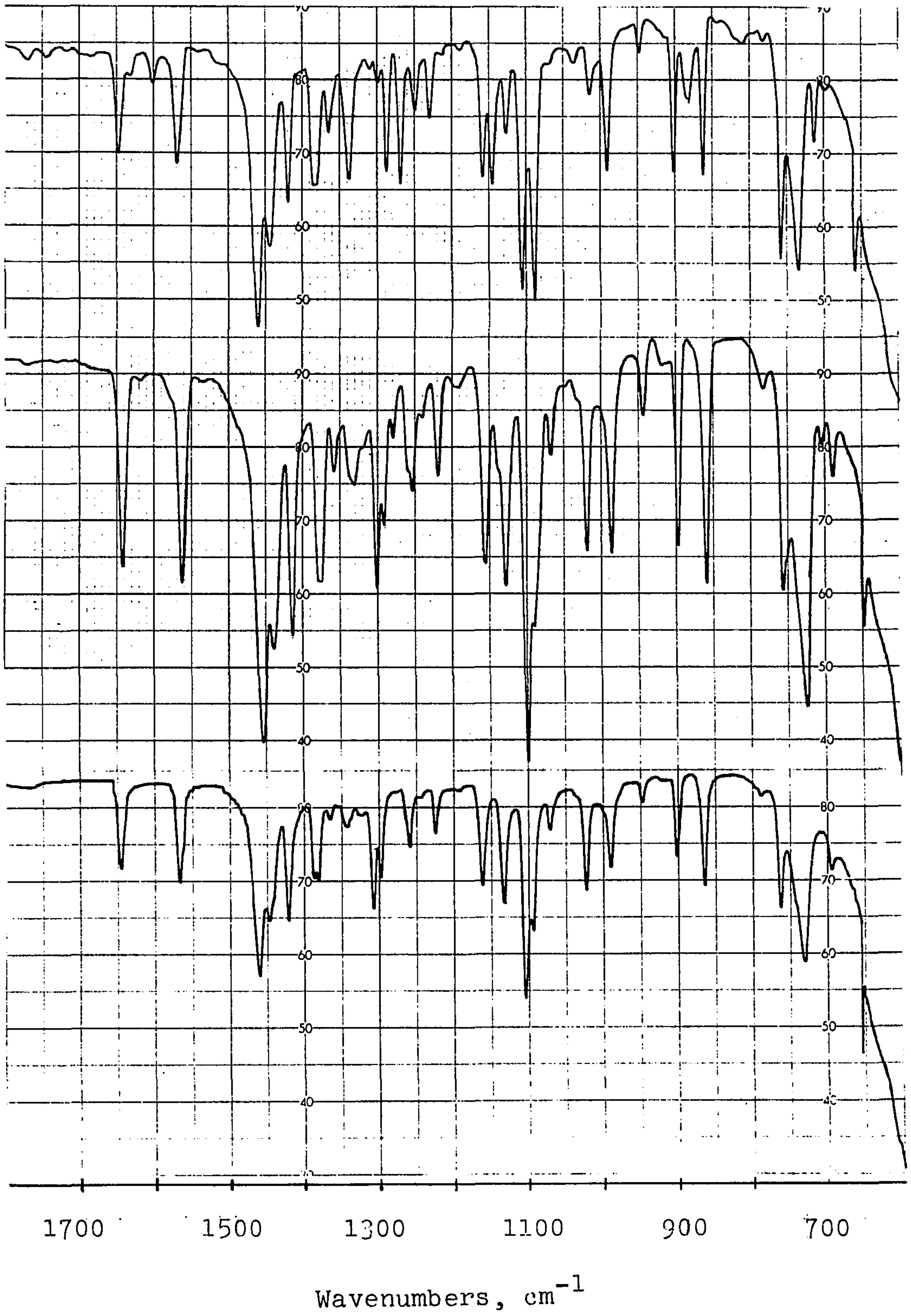

7
6
3
(PPM)
2
1
0

Figure 5. IR spectra of isomenthofuran (18) (top), a 3:1 mixture of menthofuran (17) and isomenthofuran (18) (middle), and menthofuran (17) (bottom) recorded using thin films of neat liquid

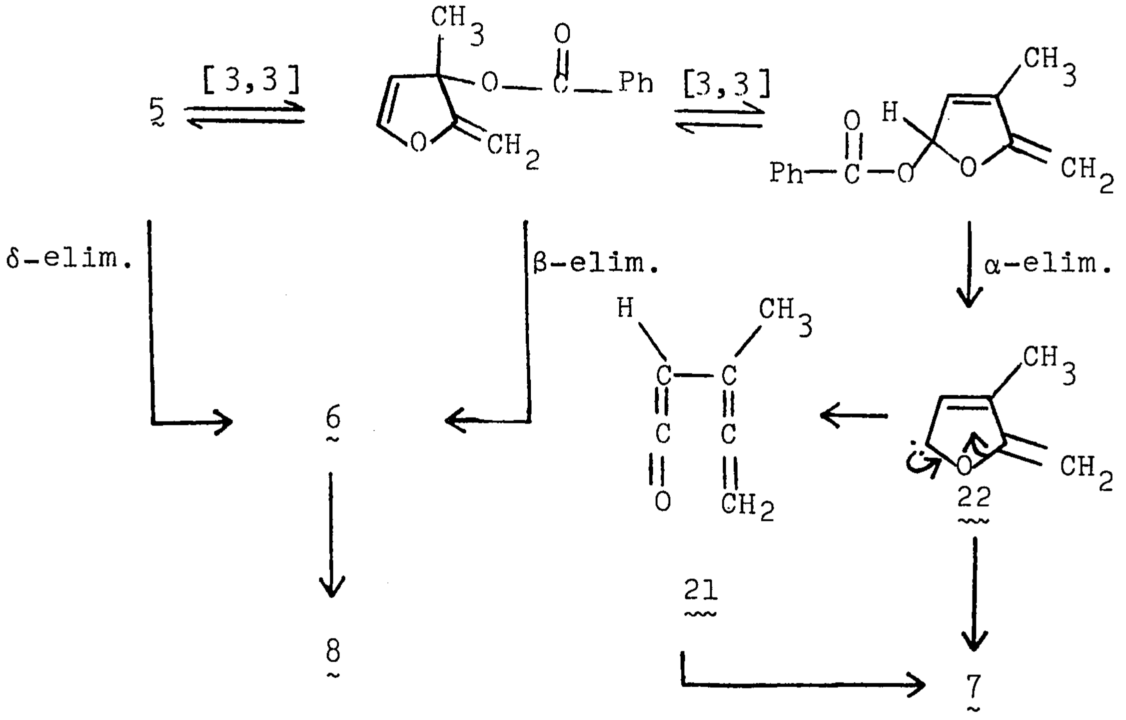


80
70
60
50
90
80
70
60
50
40
80
70
60
50
40
1700
1500
1300
1100
900
700
Wavenumbers, cm^{-1}

DISCUSSION

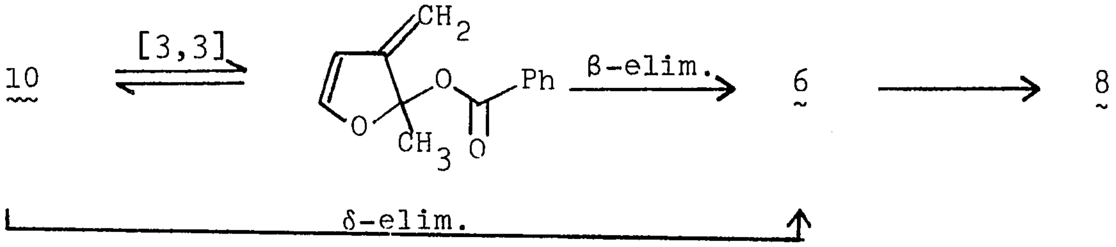
A migration mechanism was previously proposed for the conversion of furfuryl benzoate (1a) to methylenecyclobutenone (2a).[1] A set of pathways which account for the formation of the pyrolysis products from 5 is presented in Scheme I.

Scheme I

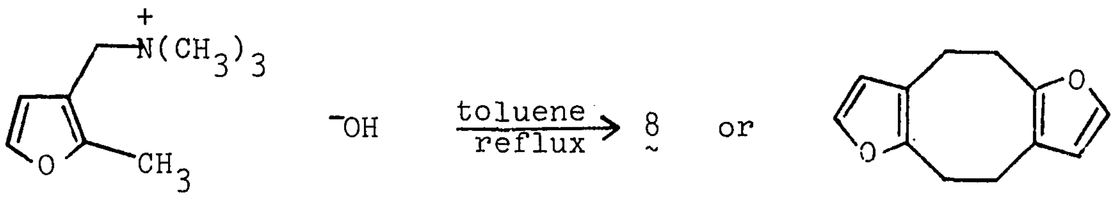


Structure 6 may be formed either directly from 5 by a δ elimination of benzoic acid, or by a two-step mechanism involving a [3,3] sigmatropic shift followed by a β elimination of benzoic acid. Product 7 can be explained by a multistep mechanism involving two [3,3] sigmatropic shifts with subsequent α elimination of benzoic acid and ring opening to form 3-methylallenylketene (21), which undergoes ring closure to form 7. Alternatively, product 7 may be formed by a direct ring contraction of carbene 22 to form 7 without involving the intermediacy of 21.

Further support for the migration mechanism was obtained from the study of the pyrolysis products formed from 2-methyl-3-furylmethyl benzoate (10). The exclusive formation of 6, which dimerized to 8 upon warming, can be explained by a direct δ elimination of benzoic acid or by a two-step mechanism involving a [3,3] shift followed by a β elimination of benzoic acid. This 1,4-elimination reaction has literature precedent in the pyrolysis chemistry of allylic$^{7-11}$ and benzylic$^{12-14}$ esters containing functional groups with δ hydrogens. In the pyrolysis of several allylic systems, the initially formed [3,3] shift products have been isolated.$^{7,10,15-20}$

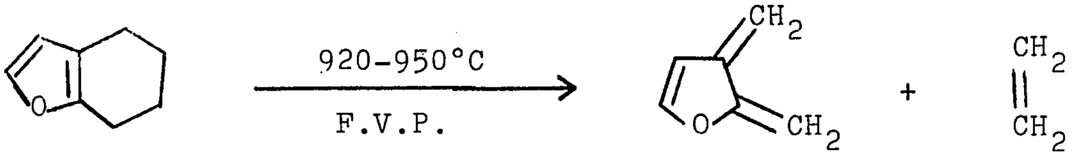


2,3-Dimethylene-2,3-dihydrofuran (6) was previously postulated as an intermediate in the liquid-phase pyrolysis of (2-methyl-3-furylmethyl) trimethylammonium hydroxide (23).[21] This reaction was reported to give one dimer of 6 possessing either structure 8 or 24.



23 24

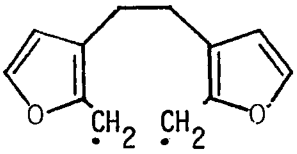
Compound (6) was also reported to be a product of the pyrolysis of 4,5,6,7-tetrahydrobenzofuran (25) at 920 to 950°C.[22] Although there was no mention of any dimerization of 6, the authors reported that several different Diels-Alder adducts were obtained in yields ranging from 20 to 50%. The inability of these workers to obtain NMR spectra for 6 and 14, when samples were warmed above -120°C, might be explained by our observation that the solubility of 6 diminishes at temperatures below -100°C and dimerization occurs rapidly. The enhanced dimerization is probably caused by increased local concentrations of 6.



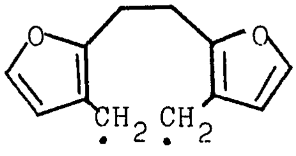
25

6

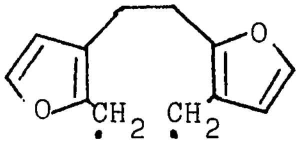
The exclusive formation of dimer 8 from 6 is readily explained by a two-step mechanism involving a diradical intermediate. There are three possible diradical intermediates: 26, 27 and 28. Intermediates 26 and 27 would lead to the formation of dimer 8, while 28 would lead to the head-to-tail dimer (24). Simple resonance considerations suggest that the radical center found in 26 is more stable than that found in 27. However, a stability difference of the two radical centers in favor of either center means that one of the symmetrical diradical intermediates (26 or 27) will be more stable than the unsymmetrical intermediate (28), which has one of each center.



26



27

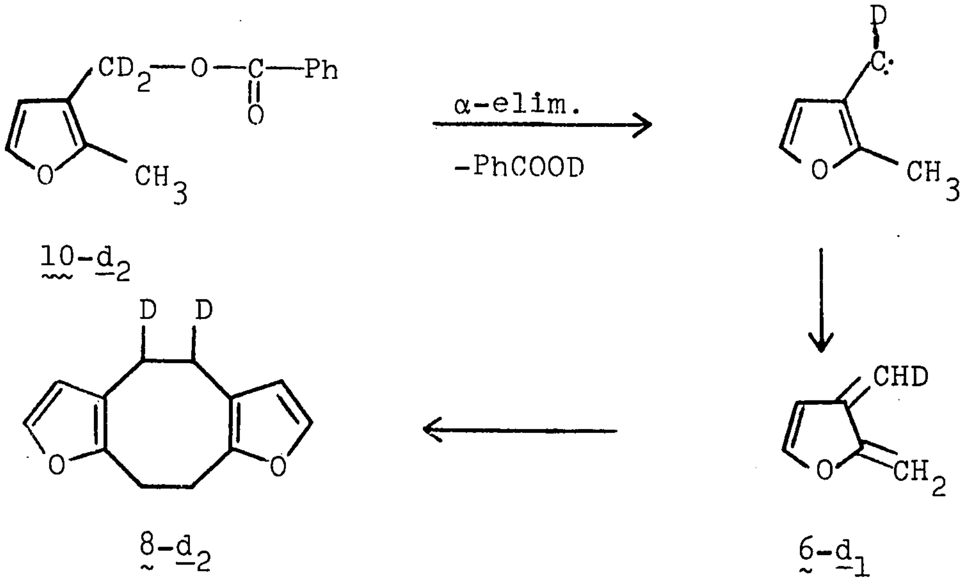


28

The mechanism of the dimerizations of 6 and 14 is analogous to that proposed for the dimerization of *ortho*-xylylene,[3f] trimethylenecyclobutane,[23] and tetramethylenecyclobutane.[24]

The 1,4-elimination mode for the loss of benzoic acid in the pyrolysis of 10 was rigorously established by studying the pyrolysis products from 10-d_2. The deuterium content of 6-d_2 and 8-d_4, determined by ^{1}H NMR analysis for 6-d_2 and by both ^{1}NMR analysis and GLC analysis for 8-d_4, rules out the possibility of a mechanism involving an initial α-elimination of benzoic acid from 10-d_2. The sample of [4+4] dimer 8-d_4 consisted of greater than 95% of species having four deuterium atoms. The observation that only ca. 0.5% of the [4+4] dimer had less than three deuterium atoms makes the α-elimination mechanism presented in Scheme II at best a minor reaction pathway.

Scheme II



$\mathbf{10}$-d_2

$\mathbf{6}$-d_1

$\mathbf{8}$-d_2

EXPERIMENTAL

Methods and Materials. The pyrolysis apparatus has been previously described.[25] ^1H NMR spectra were recorded on Varian A-60, HA-100 or Hitachi-Perkin Elmer R-20B spectrometers. ^{13}C NMR spectra were recorded on a Bruker HX-90 or a JEOL FX-90Q spectrometer. Chemical shifts are reported in parts per million (δ) from TMS. Infrared spectra were measured with a Beckman 4250 spectrophotometer. High resolution mass spectra were measured with an Associated Electronics Industries MS-902 instrument at 70 eV. Gas chromatography/mass spectral data (GLC/MS) were recorded using a Finnigan 4000 instrument with an INCOS 2300 data system at 70 eV. GLC analyses were performed using a Hewlett Packard HP 5840A instrument with a 25 meter, methylsilicone-coated capillary column. Melting points were determined with a Thomas-Hoover apparatus and are uncorrected.

A 1.6 M solution of n-butyllithium in hexane, chloroacetone, diisopropylamine, methyl acrylate and 4-methylcyclohexanone were obtained from Aldrich Chemical Co. Lithium aluminum hydride and lithium aluminum deuteride were obtained from Alpha Products. Benzoyl chloride, menthofuran, methanesulfonyl chloride and triethylamine were obtained from

Eastman Organic Chemicals. Ethyl acetoacetate and pyridine were obtained from Fisher Scientific Co. A lecture bottle of gaseous hydrogen chloride was obtained from Matheson Scientific Co. A solution of aqueous chloroacetaldehyde was obtained from Pfaltz and Bauer. 3-Methylfurfuryl alcohol[26] was prepared by the lithium aluminum hydride reduction of methyl 3-methyl-2-furoate.[27]

3-Methylfurfuryl Benzoate (5). A solution of 20.10 g of benzoyl chloride (143 mmol) in 50 mL of ether was added over a 15 min period to a stirred solution containing 16.00 g of 3-methylfurfuryl alcohol (143 mmol)[26] and 11.29 g of pyridine (143 mmol) in 100 mL of ether. The mixture was then stirred at room temperature for 4 h. After the addition of 75 mL of water, the layers were separated and the aqueous portion was extracted twice with 25 mL of ether. The combined ether layers were washed successively with 1 M hydrochloric acid (3 x 50 mL), saturated sodium bicarbonate (2 x 50 mL) and saturated sodium chloride (3 x 50 mL). After the organic layer was dried, the solvent was removed yielding the crude product, which was purified by vacuum distillation yielding 29.01 g (134 mmol; 93%) of 5: bp 110°C (0.65 mm); IR (CCl_4) 1724, 1268, 1095 cm^{-1}; ^1H NMR (CCl_4) δ 8.25-7.9 (m, 2H), 7.7-7.1 (m, 4H), 6.17 (d, J=2 Hz, 1H), 5.23 (s, 2H), 2.1 (s, 3H); high resolution mass spectrum, calcd for $C_{13}H_{12}O_3$ 216.0786, measured 216.0779.

Ethyl 2-Methyl-3-furoate.[21] A mixture of 125 mL of pyridine and 65 g (0.5 mole) of ethyl acetoacetate (distilled before use) was stirred at room temperature while 92 g (0.6 mole) of 50% aqueous chloroacetaldehyde was added over a 20 min period. The red mixture was stirred at room temperature for 4 h. After standing overnight, the layers were separated and the aqueous layer was extracted with ether (4 x 25 mL). The combined ether and organic layers were washed successively with water (4 x 25 mL) and saturated sodium chloride (3 x 25 mL). After drying ($MgSO_4$) and removal of the solvent, the crude product (49 g; 0.32 mole; 64%) was purified by vacuum distillation, yielding 40.1 g (0.26 mole; 52%) of a colorless liquid: bp 69-71°C (12 mm) [lit.[21] bp 80-85°C (16 mm)]; IR (thin film) 1730, 1618, 1530, 1310, 1242, 1195, 1105, 1045, 953, 900, 788, 742 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.21 (d, J = 2 Hz, 1H), 6.63 (d, J = 2 2 Hz, 1H), 4.28 (q, J = 7 Hz, 2H), 2.56 (s, 3H), 1.33 (t, J = 7 Hz, 3H).

2-Methyl-3-furylmethyl Alcohol.[21] To a stirred slurry of 6.24 g (0.164 mole) of lithium aluminum hydride ($LiAlH_4$) in 60 mL of dry ether ($LiAlH_4$) at 0°C was slowly added a solution of 12.61 g (0.082 mole) of ethyl 2-methyl-3-furoate in 50 mL of dry ether. After stirring the mixture for 5 h at room temperature, a standard workup[28] yielded 8.96 g (0.08 mole;

97%) of 2-methyl-3-furylmethyl alcohol: IR (thin film) 3350, 1632, 1518, 1210, 1045, 1000, 938, 892, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.19 (d, J = 2 Hz, 1H), 6.32 (d, J = 2 Hz, 1H), 4.34 (m, 2H), 3.75 (m, 1H), 2.23 (s, 3H); high resolution mass spectrum, calcd for $C_6H_8O_2$ 112.05243, measured 112.05232.

*2-Methyl-3-furylmethyl Benzoate (**10**)*. A solution of benzoyl chloride (80.7 mmol) in 50 mL of ether (dried over $LiAlH_4$) was added dropwise to a stirred solution of 2-methyl-3-furylmethyl alcohol (80.0 mmol) and triethylamine (96 mmol) in 100 mL of dry ether. After stirring the mixture for 10 h at room temperature, 100 mL of water were added and the products were isolated using the method described for the preparation of **5**. A vacuum distillation of the crude product yielded 15.9 g (73.5 mmol; 92%) of **10**: bp 88°C (0.01 mm); IR (thin film) 1720, 1625, 1600, 1515, 1270, 925 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.2-7.9 (m, 2H), 7.7-7.3 (m, 3H), 7.25 (d, J = 2 Hz, 1H), 6.41 (d, J = 2 Hz, 1H), 5.16 (s, 2H), 2.35 (s, 3H); high resolution mass spectrum calcd for $C_{13}H_{12}O_3$ 216.0786, measured 216.0783.

*2-Methyl-3-furylmethyl-α,α-$\underline{d}_2$ Benzoate (**10**-$\underline{d}_2$)*. To a stirred slurry of 1.498 g (35.7 mmol) of lithium aluminum deuteride in 10 mL of dry ether ($LiAlH_4$) at 0°C was slowly added a solution of 5.304 g (34.4 mmol) of ethyl

2-methyl-3-furoate in 15 mL of dry ether. The mixture was stirred at room temperature for 6 h and a standard workup[28] gave 3.47 g (30.4 mmol; 88.4%) of 2-methyl-3-furylmethyl-α,α-$\underline{d}_2$ alcohol: IR (thin film) 3330 (br.), 2260-2050, 1635, 1520, 1415, 1228, 1075, 1025 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.16 (d, J = 2 Hz, 1H), 6.28 (d, J = 2 Hz, 1H), 3.33 (s, 1H), 2.21 (s, 3H); high resolution mass spectrum calcd for $C_6H_6D_2O_2$ 114.06499, measured 114.06521. Without further purification 3.41 g (29.9 mmol) of the alcohol was converted to 10-$\underline{d}_2$ using the procedure described for the synthesis of 10. The benzoate was purified by column chromatography on silica gel (2% ether in hexanes) followed by distillation, yielding 5.9 g (27 mmol; 90.4%) of 10-d_2: IR (thin film) 2280-2100, 1720, 1605, 1520, 1175, 1025, 1010 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.24-7.27 (m, 5H), 7.21 (d, J = 2 Hz, 1H), 6.37 (d, J = 2 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 166.53, 151.04, 140.58, 132.89, 130.34, 129.64, 128.34, 114.52, 111.65, 11.65; high resolution mass spectrum, calcd for $C_{13}H_{10}D_2O_3$ 218.09120, measured 218.09071. Mass spectral analysis at 20 eV showed that the benzoate was >95% $\underline{d}_2$.

Ethyl 2,4-Dimethyl-3-furoate.[29] Dry hydrogen chloride was bubbled into a mixture of ethyl acetoacetate (167.0 g; 1.283 mole) and chloroacetone (154.48 g; 1.67 mole) at 0°C for 3.5 h to ensure that the solution was saturated. The solution was maintained at temperatures between -5 and 0°C for 48 h. The mixture was then poured over cracked ice in a 1 L beaker and small portions of sodium carbonate were added until the mixture was neutralized (total of 40 g). After the layers were separated, the aqueous layer was extracted with ether (4 x 50 mL). The combined ether and organic layers were washed successively with saturated sodium carbonate (4 x 50 mL) and saturated sodium chloride (4 x 50 mL). The ether solution at 0°C was treated with 600 mL (4.3 mole) of triethylamine. The mixture was stirred at 0°C for 26 h and then warmed to room temperature. After the addition of 200 mL of distilled water, the layers were separated and the aqueous layer was extracted with ether (5 x 50 mL). The combined ether layers were washed with 1 M hydrochloric acid until the washings were acidic (ca. 4 L). The organic layer was then washed successively with saturated sodium bicarbonate (5 x 100 mL) and saturated sodium chloride (3 x 100 mL). After the organic layer was dried ($MgSO_4$), the solvent was removed yielding the crude product. The crude product was purified by fractional distillation, yielding 105.74 g (0.6287 mole; 49%) of ethyl 2,4-dimethyl-3-furoate: bp 49-55°C (1.2 mm) [lit.[29a] bp 52°C (0.8 mm)]; IR (CCl_4) 1720, 1615, 1565, 1272, 1095, 1050, 937 cm^{-1}; ^1H NMR (CCl_4) 6.94 (d, J = 1.5 Hz, 1H), 4.22 (q, J = 7 Hz, 2H), 2.47 (s, 3H), 2.08 (d, J = 1.5 Hz, 3H), 1.32 (t, J = 7 Hz, 3H).

2,4-Dimethyl-3-furylmethyl Benzoate (12). To a stirred slurry of 6.3 g (166 mmol) of $LiAlH_4$ in 120 mL of dry ether ($LiAlH_4$) at 0°C was slowly added a solution of 28.10 g (167 mmol) of ethyl 2,4-dimethyl-3-furoate. The mixture was stirred at room temperature for 5 h and a standard workup[28] gave 19.7 g (156 mmol; 94%) of 2,4-dimethyl-3-furylmethyl alcohol[30]: IR (thin film) 3330 (br), 1635, 1565, 1275, 1115, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.98 (m, 1H), 4.3 (s, 2H), 3.25 (s, 2H), 2.2 (s, 3H), 1.95 (d, J = 1.5 Hz, 3H). Without further purification, the alcohol was converted to benzoate 12 in 98% yield using the method previously described. Purification by chromatography on silica gel (1% ether in hexanes) followed by distillation yielded 32.5 g (141 mmol; 85% isolated yield from ethyl 2,4-dimethyl-3-furoate) of pure 12: IR (thin film) 1715, 1598, 1575, 1450, 1265, 1170, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.2-7.9 (m, 2H), 7.7-7.2 (m, 3H), 7.07 (m, 1H), 5.15 (s, 2H), 2.31 (s, 3H), 2.02 (d, J = 1.5 Hz, 3H); ^{13}C NMR ($CDCl_3/CS_2$) δ 166.2, 151.5, 137.3, 132.7, 130.6, 129.6, 128.3, 120.7, 115.3, 57.3, 11.8, 8.2; high resolution mass spectrum calcd for $C_{14}H_{14}O_3$ 230.094298, measured 230.09448.

General Pyrolysis Procedure. The furnace was maintained at temperatures ranging between 600 and 640°C. A sample of the furylmethyl ester in a Pyrex boat was placed into the sample chamber and the system was evacuated to ca. 10^{-4} Torr.

The sample chamber was heated to ca. 70°C during the pyrolysis. A condenser cooled to ca. -20°C was inserted between the furnace and the liquid-nitrogen-cooled trap to collect the benzoic acid formed as a byproduct. During the pyrolyses, carbon disulfide and in some cases a reagent was deposited onto the trap through a side arm. Upon completion of the reaction, nitrogen was introduced into the system and the trap was warmed to -78°C. Carbon disulfide or a reagent solution at -78°C was used to rinse the walls of the trap and then the temperature was slowly raised to room temperature. The product solution was dried (Na_2CO_3), filtered and concentrated.

Pyrolysis of 3-Methylfurfuryl Benzoate (5). A 2.0 g (9.25 mmol) quantity of 3-methylfurfuryl benzoate (5) was pyrolyzed at 630°C in the normal manner. A quantitative ^1H NMR analysis of the pyrolysate using a dibromoethane standard showed the presence of 3-methyl-4-methylenecyclobutenone (7) in 21% yield and dimer 8 in 24% yield. Thick layer chromatography on silica gel plates (2000 μ) using two elutions with 20% ethyl acetate in hexanes afforded two major bands. The upper band consisted of 0.313 g (1.67 mmol; 18%) of 4H,5H,9H,10H-cycloocta[1,2-b:6,5-b']difuran (8): mp 49-52°C (lit.[21] 54-55°C); IR ($CHCl_3$) 1610, 1500, 1436, 1040, 895 cm^{-1}; ^1H NMR (CS_2) 7.16 (d, J = 2 Hz, 2H), 6.06 (d, J = 2 Hz, 2H), 3.04 (s, 4H), 2.78 (s, 4H), high resolution mass spectrum calcd for $C_{12}H_{12}O_2$ 188.08373, measured 188.08359. The lower band consisted of 3-methyl-4-methylenecyclobutenone (7) (0.139 g; 1.48 mmol; 16%): IR (CS_2) 1779 cm^{-1}; ^1H NMR (CS_2) δ 6.86 (m, 1H), 5.02 (m, 1H), 4.70 (m, 1H), 2.34 (d, J = 1.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 187.68, 186.18, 159.65, 149.70, 95.34, 13.98, GLC/MS (70 eV) m/e (% base peak) 96.00 (0.04), 95.00 (2.54), 94.00 (42.38), 66.00 (85.28), 65.00 (55.38), 63.00 (12.95), 51.00 (39.44), 50 (27.27), 39.00 (100.00), 38.00 (23.11).

Pyrolysis of 2-Methyl-3-furylmethyl Benzoate (10). A 1.64 g quantity (7.6 mmol) of 10 was pyrolyzed at 630°C in the normal manner. The pyrolysate was collected in carbon disulfide, dried (Na_2CO_3), and concentrated. GLC and ^1H NMR analyses of the crude product mixture indicated that dimer 8 was the major product formed, along with benzoic acid. The oily product mixture was purified by sublimation at 0.15 mm with a bath temperature between 90 and 115°C yielding 0.364 g (1.93 mmol; 51%) of a white powder: 4H,5H,9H,10H-cycloocta[1,2-b:6,5-b']difuran (8), mp 53-53.5°C (lit.[21] 54-55°C); IR ($CHCl_3$) 1615, 1510, 1440, 1045, 892 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.12 (d, J = 2 Hz, 2H), 6.05 (d, J = 2 Hz, 2H), 3.00 (s, 4H), 2.74 (s, 4H); ^{13}C NMR ($CDCl_3$) δ (coupling observed in gated decoupled spectrum), 149.85 (s), 139.72 (d, J = 199.6 Hz), 117.94 (s), 113.44 (d, J = 172.1 Hz), 25.79 (t, J = 126.3 Hz), 24.87 (t, J = 127.6 Hz); high resolution mass spectrum calcd for $C_{12}H_{12}O_2$ 188.08373, measured 188.08368.

2,3-Dimethylene-2,3-dihydrofuran (6). A 0.3837 g (1.77 mmol) quantity of 2-methyl-3-furylmethyl benzoate (10) was pyrolyzed at 635°C in the normal manner. During the pyrolysis, 2 mL of 1:1 $CS_2/CDCl_3$ was deposited onto the product trap. After the reaction was finished, the trap was warmed to -78°C and 2 mL of 1:1 $CS_2/CDCl_3$ at -78°C was used to rinse the walls of the trap. After transferring some of the product solution to NMR tubes at -78°C, the ^1H and ^{13}C NMR spectra were recorded, indicating the presence of 6: ^1H NMR (1:1 $CS_2/CDCl_3$, -60°C) δ 6.68 (m, 1H), 5.73 (m, 1H), 5.17 (m, 1H), 4.90 (s, 1H), 4.75 (d, J = 1.1 Hz, 1H), 4.58 (m, 1H); ^{13}C NMR (1:1 $CS_2/CDCl_3$, -60°C), δ 157.62 (s), 148.30 (d, J = 199.6 Hz), 139.63 (s), 107.61 (d, J = 177 Hz), 102.09 (t, J = 161.7 Hz), 85.08 (t, J = 162.4 Hz). Upon warming above -40°C, 6 dimerized, forming 8. Quantitative ^1H NMR analysis using a dichloroethane standard indicated that 98.5% of 6 was converted to 8 upon warming the sample to room temperature. GLC analysis indicated that the product mixture consisted of 93.8% of the [4+4] dimer 8 and 4.98% of two [4+2] dimers (3.2.:1 ratio; structure not determined).

Pyrolysis of 2-Methyl-3-furylmethyl-α,α-d_2 Benzoate (10-d_2). A 0.431 g (2.0 mmol) quantity of (10-d_2) was pyrolyzed in the normal manner. The pyrolysate was collected in 4 mL of 1:2 $CS_2/CDCl_3$ and NMR spectral data were recorded at low temperature for 6-d_2: ^1H NMR (1:2 $CS_2/CDCl_3$, -60°C) δ 6.73 (d, J = 1.5 Hz, 1H), 5.78 (m, 1H), 4.85 (d, J = 1.5 Hz, 1H), 4.65 (m, 1H); ^{13}C NMR (1:2 $CS_2/CDCl_3$m -60°C) δ 157.86, 148.55, 139.55, 107.75, 85.22. Upon warming to room temperature 6-d_2 was converted to 8-d_4: ^1H NMR (1:2 $CS_2/CDCl_3$) δ 7.05 (d, J = 2 Hz, 2H), 6.00 (d, J - 2 Hz, 2H), 3.00 (s, 4H): ^{13}C NMR ($CDCl_3$) δ 149.9 (s), 139.7 (d, J = 200 Hz), 117.7 (s), 113.4 (d, J = 172 Hz), 25.8 (t, J = 129.4 Hz); GLC/MS (12 eV) d_4=95.44%, d_3=4.07%, d_2=0.49%, d_1=0.002%.

Diels-Alder Reaction of 6 with Methyl Acrylate. A 0.2708 g (1.25 mmol) quantity of 10 was pyrolyzed at 620°C. A solution of 10 mL of methyl acrylate in 10 mL of carbon disulfide was deposited into the trap during the pyrolysis. After the reaction was finished, the trap was warmed to -30°C and stirred for 2 h. The product mixture was then warmed to room temperature, dried (Na_2CO_3) and concentrated. Purification with a molecular-distillation apparatus yielded 0.1670 g (0.93 mmol, 74.14%) of the Diels-Alder adducts 9: IR ($CHCl_3$), 1735, 1610, 1510, 1445, 1255, 1200, 1175, 1108, 860 cm^{-1};

^{1}H NMR (CS_2) 7.09 (d, J = 2 Hz, 1H), 6.02 (d, J = 2 Hz, 1H), 3.59 (s, 3H), 2.92-1.55 (m, 7H); high resolution mass spectrum calcd for $C_{10}H_{12}O_3$ 180.078648, measured 180.078683.

Pyrolysis of 2,4-Dimethyl-3-furylmethyl Benzoate (12). A 3.01 g quantity (13.1 mmol) of 12 was pyrolyzed at 620°C in the normal manner. The pyrolysate was collected in 25 ml of carbon disulfide, dried (Na_2CO_3) and concentrated, yielding a clear, viscous liquid. Column chromatography on silica gel (hexanes as eluant) gave 0.70 g (3.2 mmol; 49.6%) of 3,6-dimethyl-4*H*,5*H*,9*H*,10*H*-cycloocta[1,2-b:6,5-b']difuran (13): IR ($CHCl_3$) 1630, 1565, 1440, 1382, 1132, 1077, 860 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.02 (m, 2H), 3.07 (s, 4H), 2.73 (s, 4H), 1.92 (d, J = 1.54 Hz, 6H); ^{13}C NMR (1:1 $CS_2/CDCl_3$) 150.06 (s), 136.57 (d, J = 198 Hz), 120.97 (s), 118.32 (s), 26.22 (t, J = 127 Hz), 22.43 (t, J = 128 Hz), 8.18 (q, J = 127 Hz); high resolution mass spectrum calcd for $C_{14}H_{16}O_2$ 216.11503, measured 216.11543.

4-Methyl-2,3-dimethylene-2,3-dihydrofuran (14). A 0.41 g quantity (1.8 mmol) of 12 was pyrolyzed at 620°C and the pyrolysate was isolated using the procedure previously described for 6. The low temperature ^{1}H and ^{13}C NMR spectra indicated the presence of 14: ^{1}H NMR (CS_2, -60°C) δ 6.61

(m, 1H), 5.27 (m, 1H), 4.84 (m, 2H), 4.65 (m, 1H), 1.89 (d, J = 1.5 Hz, 3H); ^{13}C NMR (1:1 $CS_2/CDCl_3$, -72°C) δ 158.41, 144.38, 141.99, 115.12, 99.95, 85.00, 7.86. Upon warming above -30°C, 14 dimerizes to 13.

Diels-Alder Reaction of 14 with Methyl Acrylate. A 2.38 g quantity (10.3 mmol) of 2,4-dimethyl-3-furylmethyl benzoate (12) was pyrolyzed at 640°C. The pyrolysate was collected in 40 ml of a 1:1 mixture of methyl acrylate in carbon disulfide at -78°C. The product mixture was then slowly warmed to room temperature, dried (Na_2CO_3) and concentrated. Chromatography on silica gel (5% ether in hexanes) yielded 1.57 g (8.06 mmol; 78%) of the Diels-Alder adducts (15 and 16) separated from 0.0414 g (0.19 mmol; 3.7%) of dimer 13. For 15 and 16: IR (thin film) 1735, 1635, 1568, 1187, 1160, 1035, 895 cm^{-1}; ^1H NMR (CS_2) δ 6.94 (m, 1H), 3.62 (s, 3H), 2.8-1.5 (m, 10H); high resolution mass spectrum calcd for $C_{11}H_{14}O_3$ 194.094298, measured 194.09435.

Preparation of a Mixture of Menthofuran (17) and Isomenthofuran (18). To a stirred slurry of $LiAlH_4$ (0.2 g; 5.3 mmol) in 10 ml of dry ether ($LiAlH_4$) at 0°C, was added a solution of 15 and 16 (1.00 g; 5.2 mmol) in 15 ml of dry ether. After stirring the mixture for five h at room temperature, a standard workup[21] gave 0.79 g (4.8 mmol; 92%) of a mixture of the isomeric alcohols: IR (thin film) 3370 (br.), 1655, 1570, 1422, 1045, 870 cm^{-1}; ^{1}H NMR (CS_2) δ 6.82 (m, 1H), 3.92 (s, 1H), 3.40 (d, J = 5.5 Hz, 2H), 2.55-1.0 (m, 10H). Without further purification the isomeric alcohols were converted to the corresponding mesylates using a standard procedure.[31] For the mesylates: IR (thin film) 1645, 1560, 1425, 1355, 1175, 885, 735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.1 (m, 1H), 4.2 (distorted d, J=5.5 Hz, 2H), 3.04 (s, 3H), 2.9-1.0 (m, 10H). Due to their instability, the mesylates were immediately reduced without further purification. A solution of the mesylates in 5 mL of dry THF ($LiAlH_4$) was slowly added to a slurry of $LiAlH_4$ (0.5 g; 13 mmol) in 10 mL of THF at 0°C. After refluxing the mixture for 26 h, 50 mL of ether was added and a standard workup[28] was employed yielding 0.56 g (3.8 mmol) of crude product. A short path distillation gave 0.25 g (1.7 mmol, 35%) of an inseparable mixture of menthofuran (**17**) and isomenthofuran (**18**): bp 34-49°C (bath temp.) (0.05 mm); IR (thin film) 1645, 1565, 1418, 1100, 1090, 1020, 900, 860, 710, 695 cm^{-1}; ^{1}H NMR (CS_2) δ 6.8 (m, 1H), 3.0-0.8 (m, 7H), 1.93 (d, J=1.5 Hz, 3H), 1.05 (distorted d, J=5.5 Hz, 3H); high resolution mass spectrum calcd for $C_{10}H_{14}O$ 150.10447, measured 150.10425. A ^{13}C NMR analysis of the product mixture indicated that the ratio of **17** to **18** was 3.3 to 1 (average of 2 runs).

Menthofuran (17) (3,6-Dimethyl-4,5,6,7-tetrahydrobenzofuran). A commercial sample was purified by distillation to give an analytical sample of 17: bp 26-27°C (0.1 mm); IR (thin film) 1645, 1565, 1422, 1105, 1095, 1025, 905, 865, 695 cm^{-1}; ^1H NMR (CS_2) δ 6.83 (m, 1H), 3.0-0.8 (m, 7H), 1.84 (d, J = 1.5 Hz, 2H), 1.0 (distorted d, J - 5.5 Hz, 3H); ^{13}C NMR (1:1 $CS_2/CDCl_3$) δ 150.3 (s), 136.8 (d, J = 198 Hz), 119.2 (s), 117.1 (s), 31.5 (t, J = 127 Hz), 7.9 (q, J = 126.5 Hz); high resolution mass spectrum calcd for $C_{10}H_{14}O$ 150.10447, measured 150.10404.

2-Isopropylidene-4-methylcyclohexanone (19).[5] To a stirred solution of diisopropylamine (8.13 g; 0.08 mole) in 60 mL dry tetrahydrofuran (THF) at 0°C was slowly added 52 mL of a 1.6 M solution of n-butyllithium in hexane (0.0832 mole). The mixture was stirred at 0°C for 50 min. 4-Methylcyclohexanone (9.02 g; 0.084 mole) was added dropwise while the stirred reaction mixture was kept at temperatures below 10°C. A sun lamp was directed at the pyrex flask and 10.01 g of 2-chloro-2-nitropropane was added very slowly. After the ice bath was removed, the sun lamp was allowed to shine on the flask for 3 h, forming a cloudy, amber solution. Water (18 ml) was added and the mixture was stirred at room temperature for 9 h. The organic material was codistilled with the water during a vacuum distillation (water aspirator). The layers were separated and the aqueous layer was extracted with ether (4 x 10 mL). The combined ether and organic layers were washed successively with 15% potassium hydroxide (25 mL), 1 M hydrochloric acid (4 x 20 mL), saturated sodium bicarbonate (3 x 25 mL), and saturated sodium chloride (2 x 25 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed giving the crude product which was purified by distillation, yielding 3.86 g (0.025 mole; 31.5%) of 2-isopropylidene-4-methylcyclohexanone: bp 74-78°C (6 mm) [lit.[32] 70-71°C (1.2 mm)]; IR (thin film) 3500 (broad), 1685, 1615, 1270, 1132, 1006 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.1-0.75 (m, 16H) including δ 1.02 (distorted d, J = 5 Hz, 3H), 1.77 (s, 3H), 1.96 (s, 3H).

Preparation of Isomenthofuran (18), (3,5-Dimethyl-4,5,6,7-tetrahydrobenzofuran).[33] To a stirred mixture of 2.7 mL of concentrated sulfuric acid (48.6 mmol) in 10 mL of acetic anhydride (159 mmol) at -2°C was slowly added 6.87 g (45.2 mmol) of 2-isopropylidene-4-methylcyclohexanone (19). The reddish-brown mixture was maintained at -2°C for 26 h and then for 4 h at room temperature. After the addition of 5 mL of distilled water, the crystals were collected, washed with cold methanol and dried, yielding 3.46 g (16.2 mmol; 36%) of 2-(5'-methylcyclohexen-1'-yl)propen-1,2'-sultone (20): IR ($CHCl_3$) 1658, 1580, 1370, 1152 cm^{-1};

^{1}H NMR ($CDCl_3$) δ 6.25 (m, 1H), 2.8-0.8 (m, 13H). A 2.47 g (11.5 mmol) quantity of 20 was pyrolyzed at 640°C and 10^{-4} Torr in the normal manner by heating the sample chamber between 70 and 120°C. The pyrolysate was dissolved in ether, dried (Na_2CO_3), and concentrated. A short path distillation gave 1.31 g (8.7 mmol; 75%) of isomenthofuran (18): IR (thin film) 1645, 1567, 1415, 1100, 1085, 898, 860, 707 cm^{-1}; ^{1}H NMR (CS_2) δ 6.86 (m, 1H), 2.95-0.75 (m, 7H), 1.82 (d, J = 1.5 Hz, 3H), 1.02 (distorted d, J = 5.3 Hz, 3H); ^{13}C NMR (1:1 CS_2/$CDCl_3$) δ 150.3 (s), 136.8 (d, J = 198 Hz), 119.3 (s), 117.5 (s), 31.3 (t, J = 127 Hz), 29.5 (d, J = 123 Hz), 28.9 (t, J = 133 Hz), 22.8 (t, J = 127 Hz), 21.3 (q, J = 125 Hz), 7.9 (q, J = 127 Hz); high resolution mass spectrum calcd for $C_{10}H_{14}O$ 150.10447, measured 150.10424.

REFERENCES

1. a) Trahanovsky, W. S.; Park, M.-G. *J. Am. Chem. Soc.* 1973, 95, 5412.

   b) Trahanovsky, W. S.; Park, M.-G. *J. Org. Chem.* 1974, 39, 1448.

2. Trahanovsky, W. S.; Alexander, D. L. *J. Am. Chem. Soc.* 1979, 101, 142.

3. a) McCullough, J. J. *Acc. Chem. Res.* 1980, 13, 270.

   b) Flynn, C. R.; Michl, J. *J. Am. Chem. Soc.* 1974, 96, 3280.

   c) Migirdicyan, E.; Baudet, J. *J. Am. Chem. Soc.* 1975, 97, 7400.

   d) Tseng, K. L.; Michl, J. *J. Am. Chem. Soc.* 1977, 99, 4840.

   e) Steiner, R. P.; Miller, R. D.; Dewey, H. J.; Michl, J. *J. Am. Chem. Soc.* 1979, 101, 1820.

   f) Errede, L. A. *J. Am. Chem. Soc.* 1961, 83, 949.

4. Hikino, H.; Konno, C. *Heterocycles* 1976, 4, 817.

5. Russell, G. A.; Jawdosiuk, M.; Ros, F. *J. Am. Chem. Soc.* 1979, 101, 3378.

6. a) Treibs, W. *Chem. Ber.* 1937, 70, 85.

   b) Pallaud, R.; Berna, J. *Industrie Parfum.* 1953, 8, 154.

   c) Morel, Th.; Verkade, P. E. *Recl. Trav. Chim. Pays-Bas* 1951, 70, 35; 1948, 67, 539; 1949, 68, 619.

7. Bailey, W. J.; Barclay, R. *J. Org. Chem.* 1956, 21, 328.

8. a) Grummitt, O.; Splitter, J. *J. Am. Chem. Soc.* 1952, 74, 3924.

   b) Grummitt, O.; Mandel, Z. *J. Am. Chem. Soc.* 1956, 78, 1054.

9. Bailey, W. J.; Goossens, J. C. J. Am. Chem. Soc. 1956, 78, 2804.

10. a) Greenwood, F. L. J. Org. Chem. 1959, 24, 1735.

    b) Greenwood, F. L. J. Org. Chem. 1962, 27, 2308.

11. Clauson-Kaas, N.; Elming, N. Acta Chem. Scand. 1952, 6, 560.

12. Trahanovsky, W. S.; Morello, M. J. "Abstracts of Papers", 178th National Meeting of the American Chemical Society, Washington, D.C., Sept. 1979, American Chemical Society: Washington, D.C., 1979; PETR 46.

13. Morello, M. J. M.S. Thesis, Iowa State University, Ames, Iowa, 1980.

14. Cristol, S. J.; Barasch, W.; Tieman, C. H. J. Am. Chem. Soc. 1955, 77, 583.

15. Marvell, C. S.; Brace, N. O. J. Am. Chem. Soc. 1948, 70, 1775.

16. Landor, P. D.; Landor, S. R. J. Chem. Soc. 1956, 1015.

17. Heilbron, I. M.; Jones, E. R. H.; McCombie, J. T.; Weedon, B. C. J. Chem. Soc. 1945, 88.

18. Burton, H. J. Chem. Soc. 1928, 1650.

19. Balfe, M. P.; Kenyon, J. Trans. Faraday Soc. 1941, 37, 721.

20. Braude, E. A.; Turner, D. W.; Waight, E. S. J. Chem. Soc. 1958, 2396, 2404.

21. Winberg, H. E.; Fawcett, F. S.; Mochel, W. E.; Theobald, C. W. J. Am. Chem. Soc. 1960, 82, 1428.

22. Jullien, J.; Pechine, J. M.; Perez, F.; Piade, J. J. Tetrahedron Lett. 1979, 3079.

23. Martin, H.-D.; Mayer, B. Tetrahedron Lett. 1979, 2351.

24. Griffen, G. W.; Peterson, L. I. J. Am. Chem. Soc. 1963, 85, 2268.

25. Trahanovsky, W. S.; Ong, C. C.; Pataky, J. G.; Weitl, F. L.; Mullen, P. W.; Clardy, J. C.; Hansen, R. S. *J. Org. Chem.* 1971, 36, 3575.

26. Elliot, M.; Janes, N. F.; Pearson, B. C. *Pestic. Sci.* 1971, 2, 243.

27. Burness, D. M. "Organic Syntheses", Coll. Vol. IV; Wiley: New York, 1963; p 649.

28. Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 584.

29. a) Alexander, E. R.; Baldwin, S. *J. Am. Chem. Soc.* 1951 73, 356.

    b) Feist, E. *Chem. Ber.* 1902, 35, 1537, 1545.

    c) Benary, E. *Chem. Ber.* 1911, 44, 489, 493.

    d) Howes, P. D.; Stirling, C. J. M. *Org. Syn.* 1973, 53, 1.

30. Novitskii, K. Y.; Khachaturova, G. T.; Bairamova, N. E.; Yur'ev, Y. K. *Khim. Geterotsikl. Soedin.* 1966, 835.

31. Crossland, R. K.; Servis, K. L. *J. Org. Chem.* 1970, 35, 3195.

32. Wolinsky, J.; Senyek, M.; Cohen, S. *J. Org. Chem.* 1965, 30, 3207.

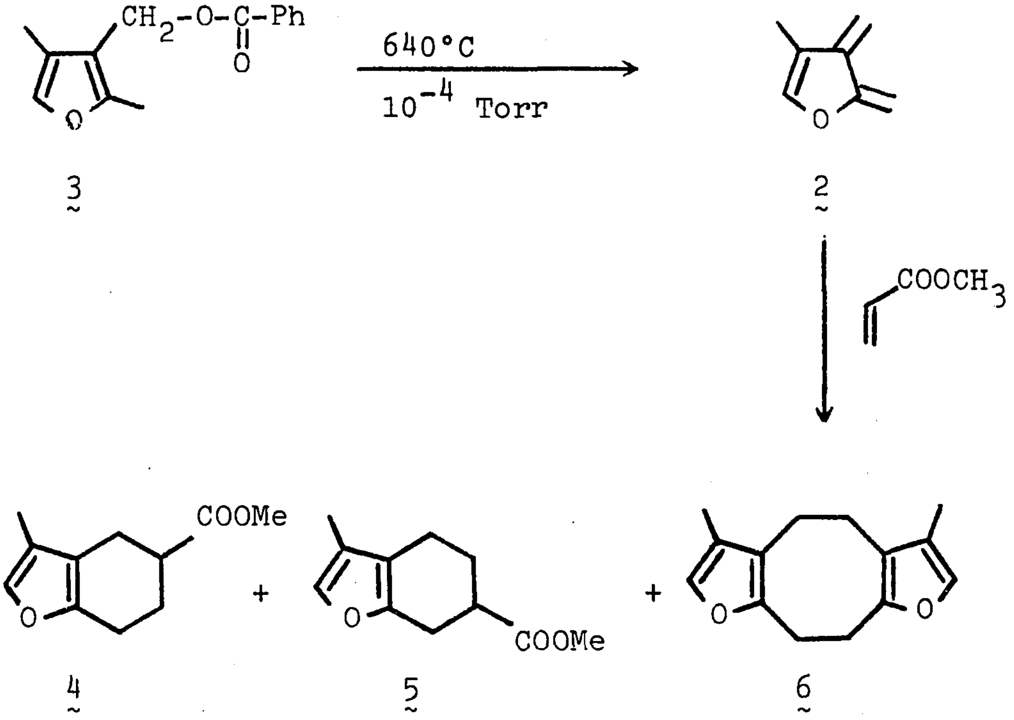
33. Garst, M. E.; Spencer, T. A. *J. Org. Chem.* 1974, 39, 584.

SECTION II. CHELATROPIC ADDITION OF SULFUR DIOXIDE TO 2,3-BIS(METHYLENE)-2,3-DIHYDRO-4-METHYLFURAN

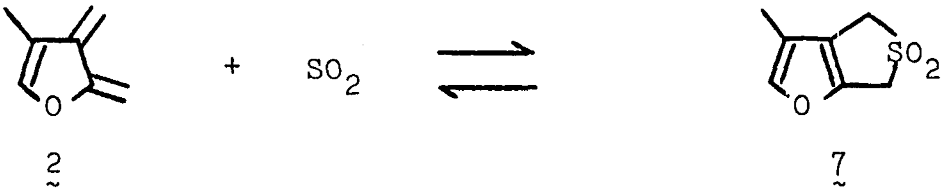
INTRODUCTION

The high reactivity of 2,3-bis(methylene)-2,3-dihydrofuran (1) as a diene suggested that the Diels-Alder reactions of 1 would be a direct method for obtaining the furanocyclohexane ring skeleton.[1,2] Since a large number of sesquiterpenes contain a furanocyclohexane unit with a methyl group on the furan ring,[3] the Diels-Alder reactions of 2,3-bis(methylene)-2,3-dihydro-4-methylfuran (2) were investigated.[1] When a large excess of methyl acrylate was added to the product trap during the pyrolysis of 2,4-dimethyl-3-furylmethyl benzoate (3), good yields of the Diels-Alder adducts 4 and 5 were obtained (64-75%) along with small amounts of [4+4] dimer 6 (2-9%) and substantial amounts of a white, insoluble polymer.[1] The ratio of 4 to 5 was determined to be 3.0 to 1 using ^{13}C NMR techniques.

Only reactive dienophiles such as methyl acrylate, acrolein and methyl vinyl ketone were observed to react with 2 at temperatures low enough (-30°C) to minimize the dimerization of 2.[1] In order to improve the reactions of 2 with dienophiles, a method of generating low concentrations of 2 at temperatures higher than -30°C in the presence of the dienophile was desired. One approach toward solving this problem involves the use of a reversible addition of sulfur



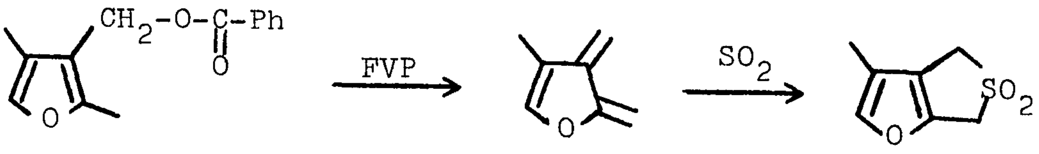
dioxide to 2. Triene 2 would be converted to sulfone 7 by adding a large excess of sulfur dioxide to a solution of 2 at -78°C. Compound 2 would later be regenerated in low concentration by heating a solution of sulfone 7.



Many examples of thermal additions of sulfur dioxide to 1,3-dienes have been reported.[4-9] The reverse reaction, involving the preparation of 1,3-dienes by the elimination of sulfur dioxide from 2,5-dihydrothiophene-1,1-dioxides, has also been studied in detail.[8-20]

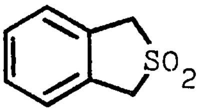
RESULTS

A solution of 2,3-bis(methylene)2,3-dihydro-4-methylfuran **2** was prepared by pyrolyzing 2,4-dimethyl-3-furylmethyl benzoate (**3**) at 640°C and 10^{-4} Torr. The benzoic acid formed as a byproduct was collected onto a condenser at ca. -30°C which was inserted between the furnace and the liquid-nitrogen-cooled trap. The volatile products, which were deposited into the liquid-nitrogen-cooled trap, were dissolved in 30 mL of methylene chloride at -78°C. A large excess of sulfur dioxide was condensed into the product trap and the temperature was gradually warmed to 10°C over a 24 h period. Removal of the excess sulfur dioxide and the solvent yielded a 66% yield (average of five runs) of the sulfone **7** as a labile, yellowish-brown solid.

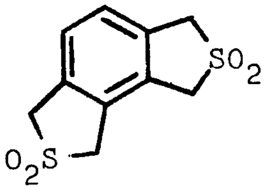


3 **2** **7**

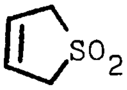
The structure of sulfone **7** was indicated by its spectral properties. The ^1H NMR spectrum of **7** included a one-hydrogen multiplet at δ 7.25 for the furan ring hydrogen, two-hydrogen multiplets at δ 4.22 and 4.14 for the methylene hydrogens and a three-hydrogen doublet (J = 1.5 Hz) for the methyl group. The chemical shifts observed for the methylene hydrogens of 7 correlated well with the chemical shifts observed for the methylene hydrogens of the benzene analog 8 (δ 4.37)[8] and the methylene hydrogens of the bis(sulfone) 9 (δ 4.53).[13] The IR spectrum of 7 included sharp, intense signals at 1322 and 1111 cm^{-1} for the asymmetric and symmetric



8



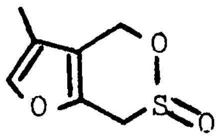
9



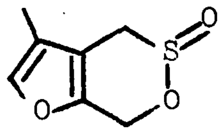
10

stretching frequencies characteristic of a sulfone. The observed IR signals correlated well with the corresponding signals reported for butadiene sulfone (10) at 1310 and 1130 cm^{-1}, respectively.[21]

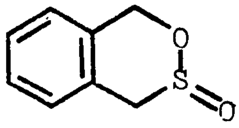
Although the reaction of sulfur dioxide with 2,3-bis(methylene)-2,3-dihydro-4-methylfuran (2) could in principle form either one or both of the sulfinate esters 11 or 12, in addition to the isolated sulfone 7, there was no IR or ^{1}H NMR spectral evidence indicating the presence of 11 or 12 in the product mixture. The ^{1}H NMR spectrum of the



11



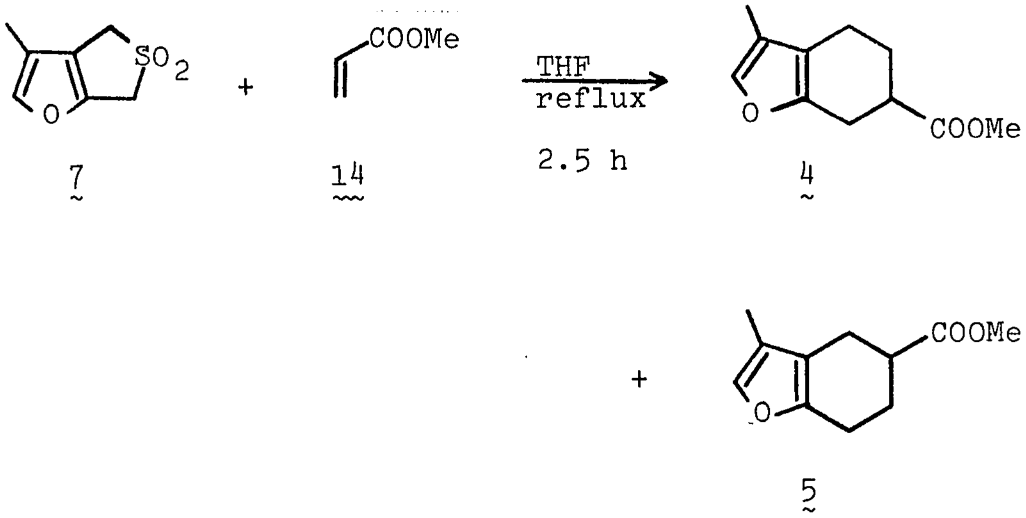
12



13

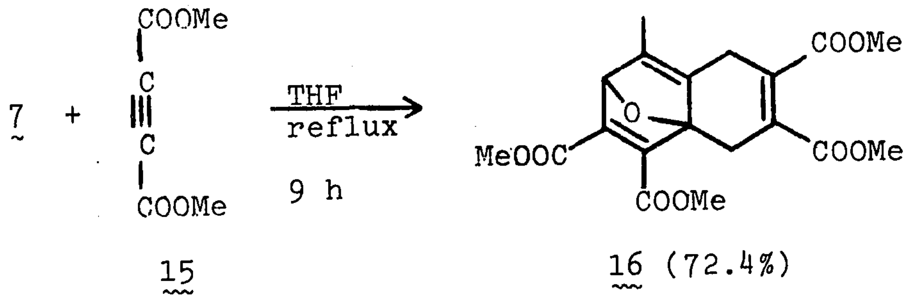
benzene analog 13 of 11 and 12 included an AB pattern at δ 3.51 and 4.37 (J = 15 Hz) for the methylene group attached to the sulfur and an AB pattern at δ 4.91 and 5.27 (J = 14 Hz) for the methylene group attached to the oxygen. The IR spectrum of 13 included a signal at 1105 cm^{-1} (S=O).[9]

The utility of sulfone 7 as a precursor to 2,3-bis-(methylene)-2,3-dihydro-4-methylfuran (2) was tested by heating solutions of 7 in the presence of an excess of methyl acrylate (14). When a tetrahydrofuran (THF) solution of 7 which also contained 2.6 equivalents of 14 was heated at its reflux temperature for 2.5 h, the only major products isolated were the Diels-Alder adducts 4 and 5. All of the starting sulfone 7 reacted under these conditions. Experiments varying the amount of methyl acrylate present in the reaction mixtures showed that in tetrahydrofuran, the presence of 2.5 equivalents of methyl acrylate was necessary to preclude formation of the [4+4] dimer 6. Under these

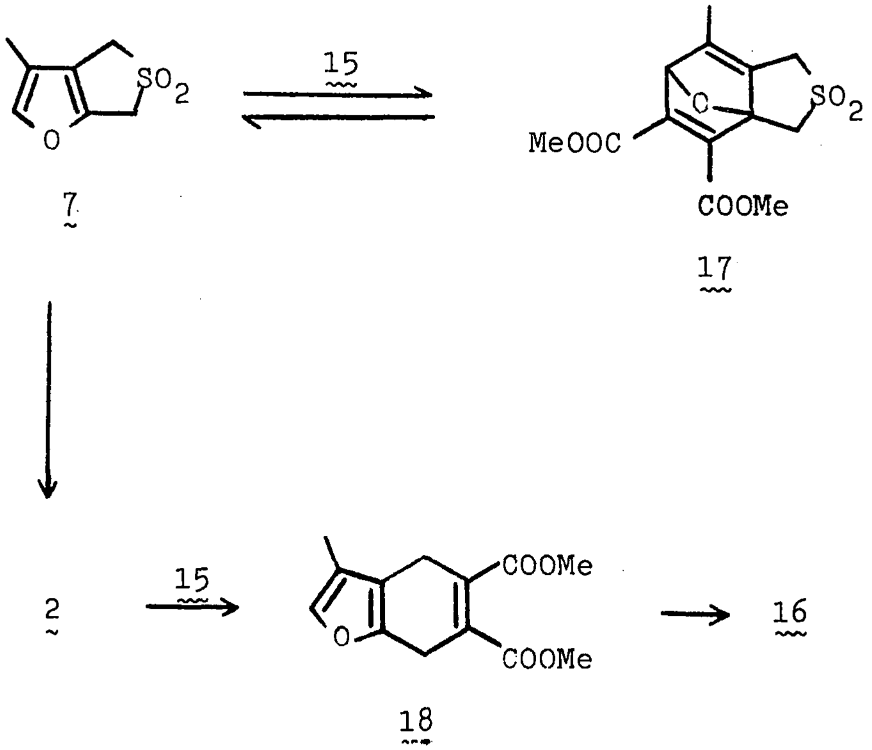


reaction conditions, a 62.7% yield of the Diels-Alder adducts 4 and 5 was obtained. The ratio of 4 to 5 was determined to be 3.3 to 1 using the ^{13}C NMR method previously reported.[1]

The use of dienophiles which show greater reactivity toward dienes than that shown by methyl acrylate was investigated in order to determine if the furan ring of either the starting sulfone 7 or the initially formed Diels-Alder adduct would act as a diene in a Diels-Alder reaction. When a THF solution of sulfone 7 containing 3.1 equivalents of dimethyl acetylenedicarboxylate (15) was heated at its reflux temperature for 9 h, the only product isolated was bis(adduct) (16). There was no ^{1}H NMR

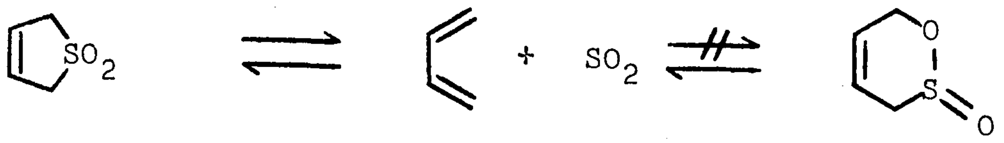


evidence indicating that a Diels-Alder reaction between **7** and **15** had taken place before the extrusion of sulfur dioxide from **7**. However, this observation does not rule out the possibility that an equilibrium takes place between sulfone **7** and adduct **17** under the reaction conditions. This equilibrium would result in the conversion of **17** to diadduct **16** via the intermediacy of **7**, **2** and **18**.



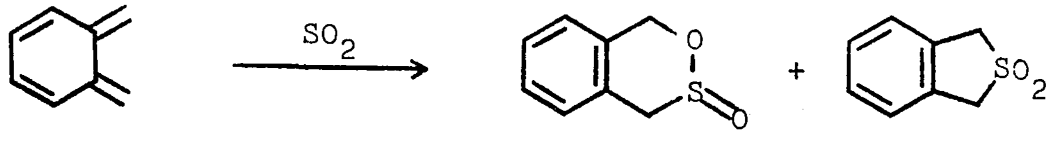
DISCUSSION

The reaction of sulfur dioxide with 1,3-butadiene can in principle form either 2,5-dihydrothiophene-1,1-dioxide (10) or 3,6-dihydro-1,2-oxathiin-2-oxide (19). Both the formation of 10 from butadiene and the reverse reaction have been studied in detail.[4,22]



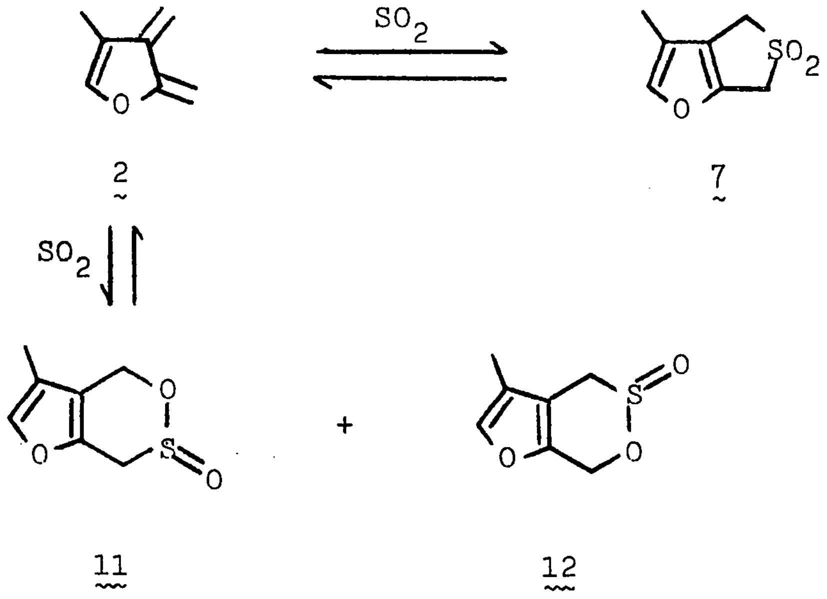
10 19

In recent years, several reactions involving the formation of cyclic sulfinate esters from 1,3-dienes have been reported.[5,8] The facile reverse reaction has also been documented.[5,8] The reaction of *ortho*-xylylene (20) with sulfur dioxide at temperatures ranging from -20 to 20°C resulted in the formation of a mixture containing a 9:1 ratio of sulfinate 13 to sulfone 8.[8] The sulfinate 13 was reported to be stable for several days at room temperature.[8,9]



20 13 8

The exclusive formation of sulfone **7** from the reaction of 2,3-bis(methylene)-2,3-dihydro-4-methylfuran (**2**) with sulfur dioxide can be explained by a concerted mechanism involving a chelatropic addition of sulfur dioxide to **2**. Although the chelatropic addition of sulfur dioxide to **2** may be favored over the Diels-Alder reaction of sulfur dioxide with **2**, the failure to detect the sulfinate esters **11** and **12** is possibly due to the instability of **11** and **12** under the reaction conditions.



The use of sulfone 7 as an alternative precursor to 2 is limited due to the extremely facile dimerization of 2 that occurs in solution under the conditions necessary to generate 2 from 7. For example, when a THF solution of 2 and ten equivalents of cyclohex-2-enone (21) was heated to its reflux temperature for 12 h, the [4+4] dimer (6) was the major product (ca. 50%) while the desired Diels-Alder adducts were formed in less than 10% yield. The high reactivity of 2 toward dimerization makes the intermolecular Diels-Alder reactions of 2 of limited use as a means of obtaining the furanocyclohexane ring skeleton.

EXPERIMENTAL

Methods and Materials. The pyrolysis apparatus has been previously described.[23] ^1H NMR spectra were recorded using Varian A-60, EM-360 or HA-100 spectrometers. ^{13}C NMR spectra were recorded using a JEOL FX-90Q spectrometer. Chemical shifts are reported in parts per million (δ) from tetramethylsilane (TMS). Infrared spectra were measured using a Beckman 4250 spectrophotometer. High resolution mass spectra were measured with an Associated Electronics Industries MS-902 instrument at 70 eV.

A sample of 2,4-dimethyl-3-furylmethyl benzoate (**3**) was prepared using the method previously described.[1] Sulfur dioxide was obtained from the Matheson Co.

3-Methyl-4*H*,6*H*-thieno[3,4-b]furan-5,5-dioxide (**7**). A 2.2234 g (0.0097 mole) sample of 2,4-dimethyl-3-furylmethyl benzoate (**3**) was pyrolyzed at 640°C and 10^{-4} Torr using the general method which was previously described.[1] During the pyrolysis, 15 mL of dichloromethane at -68°C was deposited into the liquid-nitrogen-cooled trap. A condenser cooled to ca. -20°C was inserted between the furance and the liquid-nitrogen-cooled trap to collect the benzoic acid formed as a byproduct. After all of the starting material had distilled out of the sample compartment, the apparatus was shut down under nitrogen. The trap was warmed to -78°C and then 15 mL of dichloromethane at -78°C were used to rinse the materials on the walls of the trap to the bottom. A large excess of sulfur dioxide was condensed into the trap (ca. 75 mL) and then the temperature was slowly warmed to 10°C over a 24 h period. The dark brown solution was washed with saturated sodium bicarbonate (2 x 50 mL) and saturated sodium chloride (2 x 25 mL). The organic layer was dried ($MgSO_4$), filtered and concentrated yielding 1.3394 g (0.00078 mole; 80.5%) of a labile, yellowish-brown solid 7: IR ($CHCl_3$) 1620, 1550, 1322, 1111, 1010, 988, 638 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (m, 1H), 4.22 (m, 2H), 4.14 (m, 2H), 1.98 (d, J = 1.5 Hz, 3H), high resolution mass spectrum calcd for $C_7H_8O_3S$ 172.01942, measured 172.01944.

Solution Pyrolysis of Sulfone 7 in the Presence of Methyl Acrylate (14). A mixture consisting of 0.1179 g (0.685 mmole) of 2, 0.1020 g (1.19 mmole) of methyl acrylate (14), 0.3647 g (3.44 mmole) of sodium carbonate and 1 mL of THF was heated at its reflux temperature for 2.5 h. After the mixture was cooled to room temperature and filtered, the solvent was removed yielding the crude product. Quantitative ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard indicated that a 62.7% yield of the Diels-Alder adducts 4 and 5 was obtained. Analysis of the

^{13}C NMR spectrum obtained for the product mixture, using the method previously described,[1] indicated that the ratio of **4** to **5** was 3.3 to 1. The ^{1}H NMR, ^{13}C NMR and IR spectra obtained for the mixtures of **4** and **5** were identical with the spectra previously reported for these compounds.[1]

*Solution Pyrolysis of Sulfone **7** in the Presence of Dimethyl Acetylenedicarboxylate (**15**).* A mixture consisting of 0.1152 g (0.669 mmole) of sulfone (**7**), 0.2023 g (1.42 mmole) of dimethyl acetylenedicarboxylate (**15**), 0.2246 g (2.12 mmole) of sodium carbonate and 1 mL of THF was heated at its reflux temperature for 11 h. The mixture was then cooled to room temperature and filtered. Removal of the solvent and excess dimethyl acetylenedicarboxylate in a vacuum yielded 0.19 g (0.484 mmole; 72.4%) of diadduct **16**: IR ($CHCl_3$) 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.33 (m, 1H), 4.03-3.66 (m, 12H), 3.6 (broad m, 2H), 3.25 (broad m, 2H), 1.9 (m, 3H). Attempts to further purify **16** by thick layer chromatography resulted in decomposition of the product mixture.

REFERENCES

1. Trahanovsky, W. S.; Cassady, T. J.; Woods, T. L. *J. Am. Chem. Soc.* 1981, 103, 6691.

2. Jullien J.; Pechine, J. M.; Perez, F.; Piade, J. J. *Tetrahedron Lett.* 1979, 3079.

3. Hikino, H.; Konno, C. *Heterocycles* 1976, 4, 817.

4. Turk, S. D.; Cobb, R. L. In "1,4-Cycloaddition Reactions"; Hamer, J., Ed.; Academic Press: New York, 1967; Chapter 2.

5. Heldeweg, R. F.; Hogeveen, H. *J. Am. Chem. Soc.* 1976, 98, 2341.

6. Jensen, F. R.; Coleman, W. E.; Berlin, A. J. *Tetrahedron Lett.* 1962, 15.

7. Jensen, F. R.; Coleman, W. E. *J. Am. Chem. Soc.* 1958, 80, 6149.

8. Durst, T.; Tetreault-Ryan, L. *Tetrahedron Lett.* 1978, 2353.

9. Jung, F.; Molin, M.; Van Den Elzen, R.; Durst, T. *J. Am. Chem. Soc.* 1974, 96, 935.

10. Durst, T.; Lancaster, M.; Smith, D. J. *J. Chem. Soc. Perkin Trans. I* 1981, 1846.

11. Oppolzer, W.; Roberts, D. A. *Helv. Chim. Acta* 1980, 63, 1703.

12. Vogtle, F.; Rossa, L. *Angew. Chem. Int. Ed. Engl.* 1979, 18, 515.

13. Giovannini, E.; Vuilleumier, H. *Helv. Chim. Acta* 1977, 60, 1452.

14. Mock, W. L. *J. Am. Chem. Soc.* 1966, 88, 2857.

15. McGregor, S. D.; Lemal, D. M. *J. Am. Chem. Soc.* 1966, 88, 2858.

16. Cava, M. P.; Deana, A. A. J. Am. Chem. Soc. 1959, 81, 4266.

17. Oliver, J. A.; Ongley, P. A. Chem. and Ind. 1965, 1024.

18. Cava, M. P.; Mitchell, M. J.; Deana, A. A. J. Org. Chem. 1960, 25, 1481.

19. Nicolaou, K. C.; Barnette, W. E.; Ma, P. J. Org. Chem. 1980, 45, 1463.

20. McIntosh, J. M.; Sieler, R. A. Can. J. Chem. 1978, 56, 226.

21. Pouchert, C. J. "The Aldrich Library of Infrared Spectra", 3rd ed.; Aldrich Chemical Co: Milwaukee, 1981; Volume 3, p. 531G.

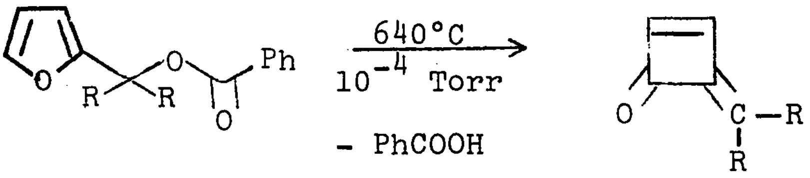
22. Mock, W. L. J. Am. Chem. Soc. 1975, 97, 3666.

23. Trahanovsky, W. S.; Ong, C. C.; Pataky, J. G.; Weitl, F. L.; Mullen, P. W.; Clardy, J. C.; Hansen, R. S. J. Org. Chem. 1971, 36, 3575.

SECTION III. FLASH VACUUM PYROLYSIS OF METHYL-SUBSTITUTED FURFURYL ESTERS

INTRODUCTION

Several years ago it was reported that furfuryl benzoate (**1a**), on pyrolysis at 640°C, gives methylenecyclobutenone (**2a**) in 40% yield along with benzoic acid and some minor products.[1] This transformation provided a synthesis of the parent structure of a series of compounds that is not readily available.[2] Methylenecyclobutenone (**1a**) was one of the missing cyclobutadiene derivatives[3] and is a potentially useful synthetic intermediate since it has a highly functionalized, cyclobutane ring.[4]



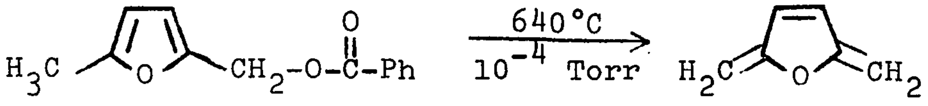
1

a, R=H

b, R=D

2 (40%)

In order to determine the scope of the reaction and to achieve a better understanding of its mechanism, the pyrolysis of a series of substituted furfuryl esters was undertaken.[5-7] A mechanism for the conversion of **1a** to **2a** was proposed on the basis of a deuterium-labeling experiment, **1b** to **2b**, and a study of the products formed from the pyrolysis of 5-methylfurfuryl benzoate (**3**) at 640°C.[5]



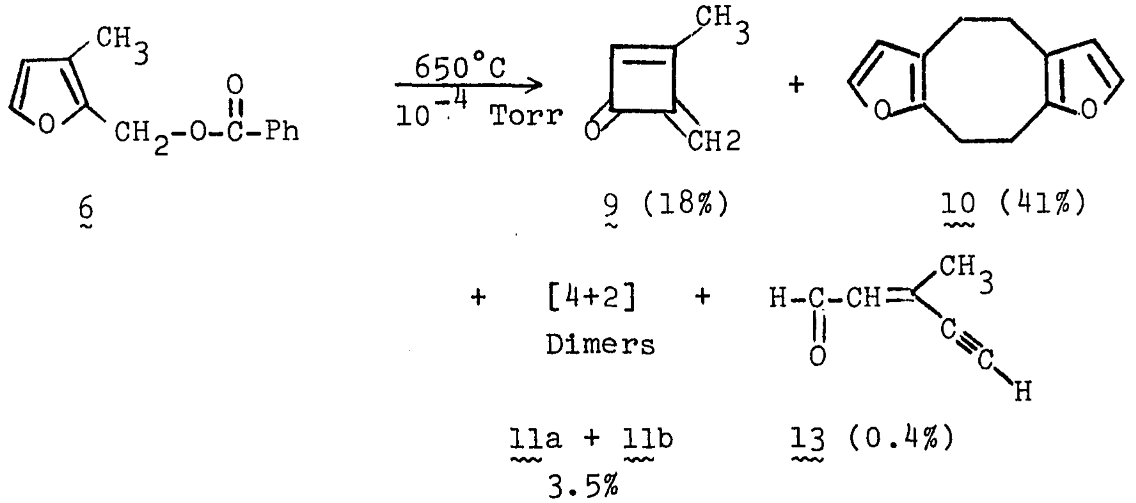
3 - PhCOOH **4**

43%

The pyrolysis of α-phenylfurfuryl acetate (**5**) formed products arising both from direct α elimination of acetic acid from **5** and from α elimination following one or more [3,3] sigmatropic shifts of the acetate group around the furan ring.[6] The pyrolysis at several temperatures of a series of methyl-substituted, furylmethyl esters was investigated in order to further test the proposed migration mechanism and to provide a synthesis of the dimethylenedihydrofurans.[7,8] These reactive trienes are the furan analogs of the *ortho*- and *para*-quinodimethanes, an actively investigated group of reactive intermediates.[9]

RESULTS

3-Methylfurfuryl benzoate (6)[7] was prepared by reducing methyl 3-methyl-2-furoate (7)[10] with lithium aluminum hydride and then esterifying the resulting 3-methylfurfuryl alcohol (8)[11] with benzoyl chloride in the presence of triethylamine. Compound 6 was pyrolyzed using the method previously reported[7] at temperatures ranging from 450 to 750°C. The major products formed were 3-methyl-4-methylene-2-cyclobutenone (9) and the [4+4] dimer 10 and [4+2] dimers 11a and 11b of 2,3-dimethylene-2,3-dihydrofuran (12).[7] There were also trace amounts of several minor products including one isomer of 3-methylpent-2-en-4-ynal (13). These products were accompanied by the formation of benzoic acid and a substantial amount of a white polymer. The product mixtures were readily separated using gas chromatography (GLC) or by thick layer chromatography. Products 11a, 11b and 13 were found to decompose readily in air or upon exposure to the TLC conditions.



6

9 (18%)

10 (41%)

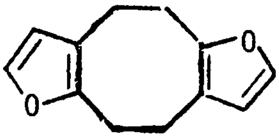
11a + 11b
3.5%

13 (0.4%)

The structure of compound 9 was indicated by its spectral properties. The ^{1}H NMR spectrum included a doublet for the methyl group at δ 2.3 (J = 1.5 Hz), multiplets for the methylene hydrogens at δ 4.7 and 5.0 and a multiplet for the ring olefinic hydrogen at δ 6.8. The ^{13}C NMR spectrum consisted of 6 peaks with appropriate chemical shifts. The IR spectrum showed an intense absorption at 1779 cm^{-1} which agrees very well with the carbonyl absorption reported for 2 (1783 cm^{-1}).[1]

The structure of dimer 10 was also determined by its spectral properties. The ^{1}H NMR spectrum exhibited four-proton singlets at δ 2.76 and 3.03 and two-proton doublets at δ 6.0 (J = 2 Hz) and δ 7.09 (J = 2 Hz). The ^{13}C NMR spectrum showed six signals, as required by the symmetry of 10, with appropriate chemical shifts.

The complete structures of the [4+2] dimers 11a and 11b were not determined due to the low yields of 11a and 11b (0.6-3.6%) and their instability. There are six possible Diels Alder dimers of 2,3-dimethylene-2,3-dihydrofuran (12). Each of the three double bonds in 12 can act as a dienophile and form two regioisomers. A GLC analysis indicated that only two [4+2] dimers were formed. The gas chromatography/mass spectral analysis (GLC/MS) indicated that the fragmentation patterns obtained for 11a and 11b were essentially superimposable with each other and with the fragmentation pattern obtained for the [4+4] dimer 10. Although the GLC/MS data does not rule out the possibility that the structure of either 11a or 11b is the head-to-tail, [4+4] dimer, the absence of ^{1}H and ^{13}C NMR peaks corresponding to the head-to-tail dimer makes it unlikely. The yields of 11a and 11b were determined by GLC. At 650°C, there was a 2:1 ratio of 11a to 11b formed in 3.5% yield.



head-to-tail
[4+4] dimer

2,3-Dimethylene-2,3-dihydrofuran (12) was shown to be the primary pyrolysis product, which dimerizes to 10, 11a and 11b upon warming, by obtaining a GLC/MS analysis of a sample of the pyrolysate from 6 kept at temperatures below -70°C. The major component of this sample showed a parent ion corresponding to the molecular formula C_6H_6O. The GLC trace also indicated smaller peaks corresponding to 9 and 13 and a minor peak corresponding to [4+4] dimer 10. When the sample was warmed to room temperature, the major component of the low temperature run had disappeared and the peak corresponding to

[4+4] dimer **10** had become the major component. Peaks corresponding to the [4+2] dimers **11a** and **11b** were also observed in the chromatogram of the sample at room temperature. In Figure 1, the gas chromatograms of the pyrolysis products of **6** recorded at -70 and 25°C are presented. There was no evidence for products resulting from a reaction between **9** and **12** in either the GLC or the spectral analyses of the pyrolysis products from **6**. The product yields from the pyrolysis of **6** at various temperatures between 450 and 750°C were determined by a combination of ^{1}H NMR and GLC analyses and are presented in Table I.

5-Methylfurfuryl benzoate (**3**)[5] was prepared by reducing 5-methylfurfural with lithium aluminum hydride and then esterifying the resulting 5-methylfurfuryl alcohol (**14**)[11] with benzoyl chloride in the presence of triethylamine. Compound **3** was pyrolyzed using the method previously reported[7] at temperatures ranging from 450 to 850°C. The only major product formed from a pyrolysis at 550°C was the expected 2,5-dimethylene-2,5-dihydrofuran (**4**)[5] (74% absolute yield); while at 850°C, the major products formed were 4-methylenecyclopent-2-enone (**15**) (21%) and phenol (5%). These products were accompanied by the formation of benzene,

Figure 1. Gas chromatograms of the pyrolysis product mixtures formed from 3-methylfurfuryl benzoate (6) recorded for a sample kept at temperatures below -70°C (top) and after warming the sample to room temperature (bottom)

(A) 2,3-dimethylene-2,3-dihydrofuran (12)
(B) 3-methyl-4-methylene-2-cyclobutenone (9)
(C) [4+2] dimers 11a and 11b
(D) [4+4] dimer 10

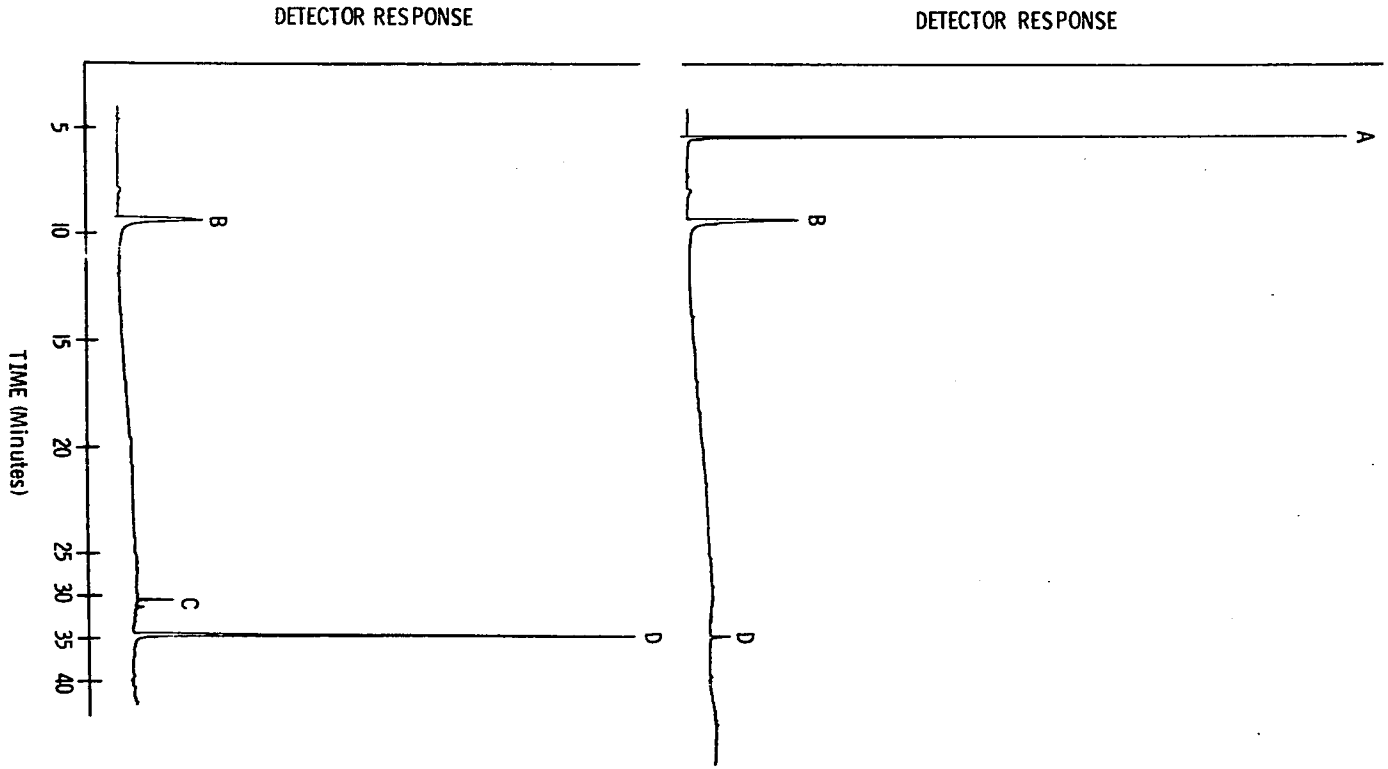

DETECTOR RESPONSE
DETECTOR RESPONSE
A
B
B
C
D
D
5
10
15
20
25
30
35
40
TIME (Minutes)

Table I. Products and yields formed from pyrolyses of 3-methylfurfuryl benzoate (6) at temperatures between 450 and 750°C

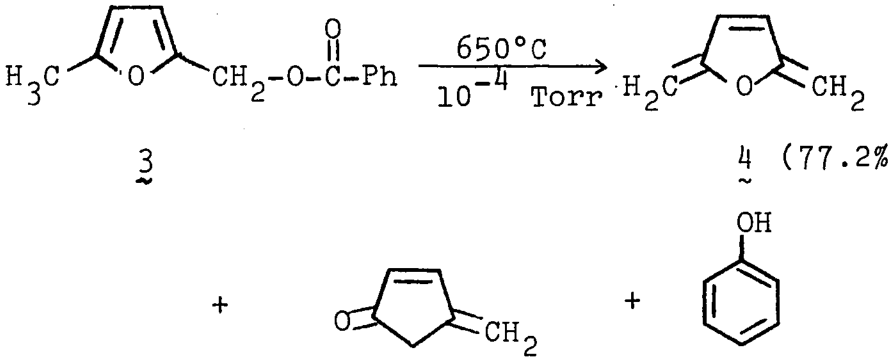
Pyrolysis Temp., °C	Products and Yields, %			Recovered Starting Material, %[a]	Ratio of 9 to (10 + 11a + 11b)
	3M-MCB[a,b]	[4+2][c] Dimers	[4+4][a] Dimers		
	9	11a + 11b	10	6	
450	1.7	0.6	7.4	84.7	0.21
550	18.1	3.6	40.2	7.3	0.42
650	18.3	3.5	40.6	----	0.42
750	5.3	1.5	15.1	----	0.32

[a] Yields were determined by ^{1}H NMR spectroscopy using 1,2-dichloroethane as an internal standard.

[b] 3M-MCB = 3-methyl-4-methylene-2-cyclobutenone.

[c] Yields were determined by GLC analysis and are absolute yields based on the absolute yield of 10 determined by ^{1}H NMR. The FID response factors for 10, 11a, and 11b are assumed to be equivalent.

trace amounts (<1%) of hex-3-en-5-yn-2-one (16), benzoic acid and substantial amounts of white, polymeric material. In addition to the major products, several unidentified products were formed at the higher pyrolysis temperatures (750 to 850°C). The product mixtures were easily separated using GLC techniques.



3

4 (77.2%)

15

0.8%

0.2%

The structure of 4 was indicated by its spectral properties. The ^{1}H NMR spectrum included two-proton doublets at δ 4.22 (J = 1.5 Hz) and 4.52 (J = 1.5 Hz) and a two-proton singlet at δ 6.42. The ^{13}C NMR spectrum consisted of three peaks, as required by the symmetry of 4, with appropriate chemical shifts. A GLC/MS analysis indicated that 4 has the molecular formula C_6H_6O.

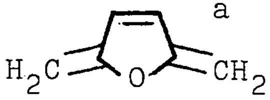
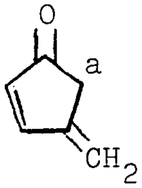
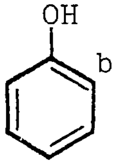
The structure of 15 was also indicated by its spectral properties. The ^{1}H NMR spectrum included a multiplet at δ 2.95 for the ring methylene group, multiplets at δ 5.28 and 5.39 for the exocyclic methylene group and doublets of multiplets at δ 6.28 (J = 6 Hz) and δ 7.7 (J = 6 Hz) for the ring olefinic hydrogens. These chemical shifts are consistent with those observed for 2-cyclopentenone [δ 7.8 (m, 1H), 6.25 (m, 1H), 2.72 (m, 2H), 2.35 (m, 2H)][12] and for 4-cyclopentene-1,3-dione [δ (1:1 $CS_2/CDCl_3$) 7.25 (s, 2H), 2.83 (s, 2H)]. The ^{13}C NMR spectrum included peaks at δ 207.8 for the carbonyl carbon, at δ 160.2 and 135.1 for the ring olefinic carbons, at δ 143.8 for the ring carbon attached to the exocyclic methylene group, at δ 114.7 for the exocyclic methylene carbon and at δ 41.62 for the ring methylene carbon. These chemical shifts agree with those observed for 4-cyclopentene-1,3-dione [δ (1:1 $CS_2/CDCl_3$) 200.2, 150.0, 41.2] and for 2-cyclopentenone (δ 208.1, 164.2, 132.9 for carbons 1,3 and 2 respectively).[13] The IR spectrum of 15 showed a strong absorption at 1705 cm^{-1}. This carbonyl band is consistent with that reported for 4-cyclopenten-1,3-dione (1710 cm^{-1}).[14] The GLC/MS data were also consistent with a molecular formula C_6H_6O.

The presence of trace amounts (<1%) of one isomer of hex-3-en-5-yn-2-one (16) in the product mixture was determined by GLC/MS analysis. Prominent peaks in the fragmentation pattern included m/e 94 for the parent ion, m/e 79 for loss of a methyl group and m/e 51 for loss of an acetyl group.

Product yields from the pyrolysis of 3 at various temperatures are presented in Table II. The maximum yield of 2,5-dimethylene-2,5-dihydrofuran (4) was obtained at a pyrolysis temperature of 650°C.

3,5-Dimethylfurfuryl benzoate (17) was prepared by reducing methyl 3,5-dimethyl-2-furoate (18)[11] with lithium aluminum hydride and then esterifying the resulting 3,5-dimethylfurfuryl alcohol (19)[11] with benzoyl chloride in the presence of triethylamine. Compound (17) was pyrolyzed at temperatures ranging from 400 to 700°C. During the pyrolyses a 1:1 mixture of carbon disulfide in deuterochloroform was codeposited into the liquid-nitrogen trap with the pyrolysate. After a known amount of dichloroethane was added as an internal standard, the trap contents were liquified by warming the trap to -78°C. ^{1}H and ^{13}C NMR spectra were recorded for the pyrolysates at temperatures below -60°C. The samples were then warmed to room temperature and ^{1}H NMR spectra were recorded. In each experiment, the product mixtures kept below -60°C consisted of 3-methyl-2,5-dimethylene-2,5-dihydrofuran (20) and

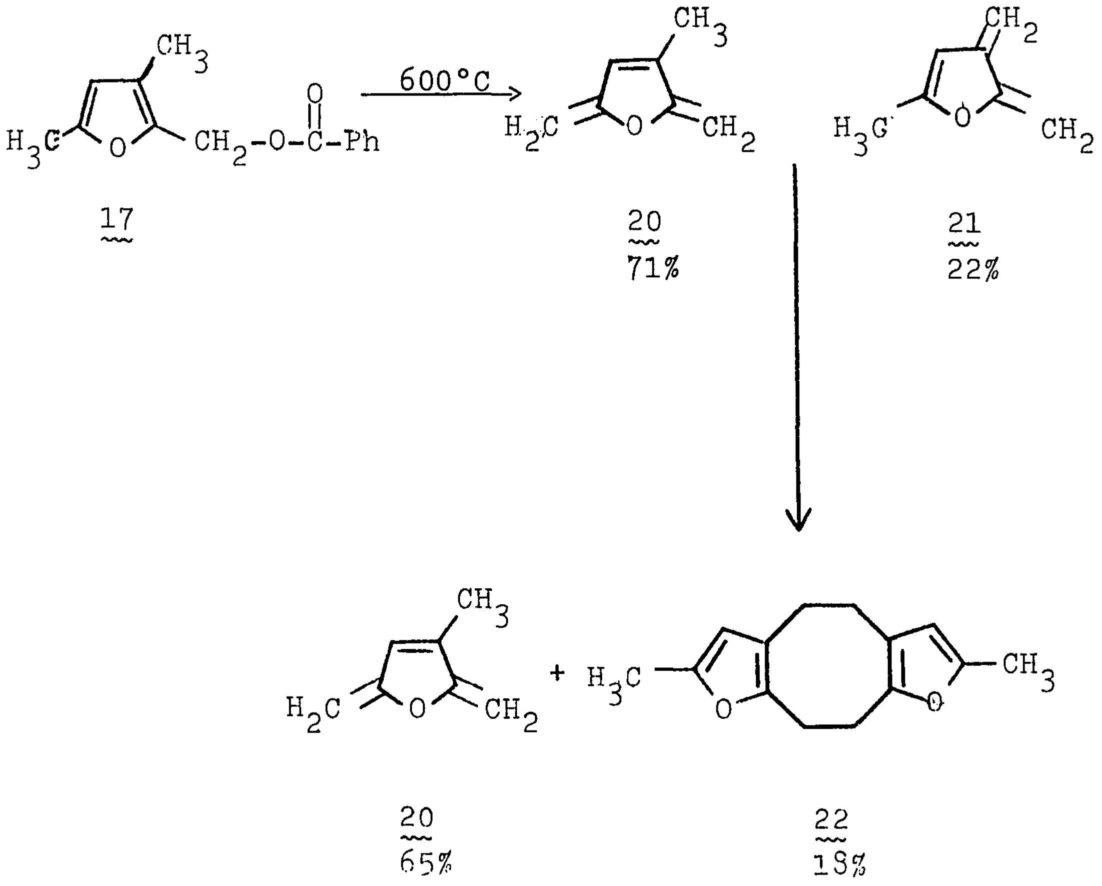
Table II. Products and yields formed from pyrolyses of 5-methylfurfuryl benzoate (3) at temperatures from 450 to 850°C

Pyrolysis Temp., °C	Products and Yields, %			Recovered Starting Material, %[a]
	 [a] 4	 [a] 15	 [b]	
450	45.1	----	---	53.9
550	74.4	----	---	<2
650	77.2	0.8	0.2	----
750	44.8	12.7	2.9	----
850	----	21.3	5.1	----

[a] Yields were determined by ^1H NMR spectroscopy using 1,2-dichloroethane as an internal standard.

[b] Yields were determined by GLC analysis and were calculated using the absolute yield of 4 determined by ^1H NMR analysis.

5-methyl-2,3-dimethylene-2,3-dihydrofuran (21). When the samples were warmed to room temperature, the product mixtures consisted mainly of 20 and 22, the head to head [4+4] dimer of 21. There was also evidence for minor amounts of two [4+2] dimers of 21.



17

20
71%

21
22%

20
65%

22
18%

The structure of 20 was indicated by spectral properties obtained for a mixture of 20 and 21. The ^{1}H NMR spectrum showed a three-proton doublet at δ 1.95 (J = 1.0 Hz) for the methyl group, two-proton multiplets at δ 4.14 and 4.44

for the exocyclic, methylene hydrogens and a multiplet at δ 6.18 for the ring, olefinic hydrogen. The ^{13}C NMR spectrum consisted of seven peaks with appropriate chemical shifts.

The structure of 21 was also indicated by spectral properties obtained for a mixture of 20 and 21. The ^{1}H NMR spectrum showed a three-proton singlet at δ 2.01 for the methyl group, multiplets at δ 4.55 (1H), 4.75 (2H) and 5.05 (1H) for the exocyclic methylene hydrogens, and a broad singlet at δ 5.44 for the ring olefinic hydrogen. These chemical shifts agree well with those reported for 2,3-dimethylene-2,3-dihydrofuran (12) and 4-methyl-2,3-dimethylene-2,3-dihydrofuran (23).[7] The production of 21 in the absence of 20 was achieved by an independent route which is described below.

The structure of 22 was also indicated by its spectral properties. The ^{1}H NMR spectrum showed a six-proton singlet at δ 2.17 for the methyl groups, four-proton singlets at δ 2.73 and 3.02 for the ring methylene hydrogens and a two-proton multiplet at δ 5.67 for the furan, ring hydrogens. The ^{13}C NMR spectrum consisted of 7 peaks, as required by the symmetry of 22, with appropriate chemical shifts.

In Figure 2, the ^{1}H NMR spectra of the pyrolysis products of 17 recorded at -60 and 35°C are presented. Product yields from runs at various temperatures are displayed in Table III.

Figure 2. ^{1}H NMR spectra of the pyrolysis products formed from 3,5-dimethyl-2-furfuryl benzoate (17) recorded at -60°C (top) and at 35°C (bottom) in 1:1 $CS_2/CDCl_3$

Top: A 3.2:1 mixture of 3-methyl-2,5-dimethylene-2,5-dihydrofuran (20) and 5-methyl-2,3-dimethylene-2,3-dihydrofuran (21)

Bottom: A 3.7:1 mixture of 20 and [4+4] dimer 22

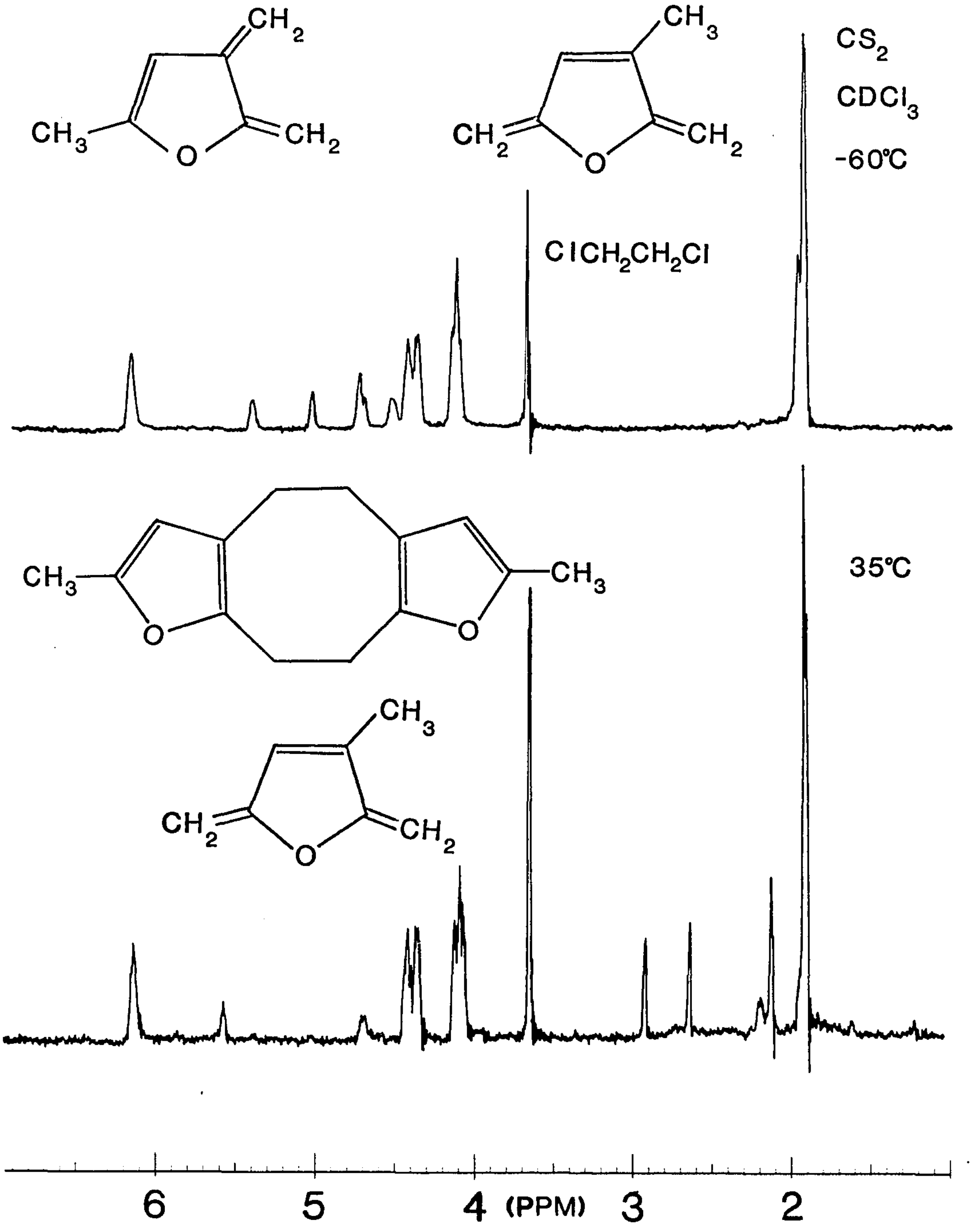

CH$_2$
CH$_3$
O
CH$_2$
CH$_3$
CH$_2$
O
CH$_2$
CS$_2$
CDCl$_3$
-60℃
ClCH$_2$CH$_2$Cl
35℃
CH$_3$
O
O
CH$_3$
CH$_3$
CH$_2$
O
CH$_2$
6
5
4
(PPM)
3
2

Table III. Products and yields formed from pyrolyses of 3,5-dimethylfurfuryl benzoate (17) at temperatures from 400 to 700°C

Pyrolysis Temp., °C	Products and Yields Determined at Temps. Below -60°C, %[a]		Products and Yields Determined at Room Temperature, %[a]		Recovered Starting Material, %[a]	Ratio of 20 to 21
	20[b]	21[c]	20[b]	22[d]	17	
400	74.3	11.9	69.0	5.5	4.8	6.3
450	75.4	17.9	72.1	10.3	---	4.2
500	---[e]	---[e]	66.5	11.1	---	---
600	70.6	22.1	64.7	17.7	---	3.2
700	41.2	12.5	46.8	11.2	---	3.3

[a] Yields were determined by ^{1}H NMR spectroscopy using 1,2-dichloroethane as an internal standard.

[b] 20 = 3-methyl-2,5-dimethylene-2,5-dihydrofuran.

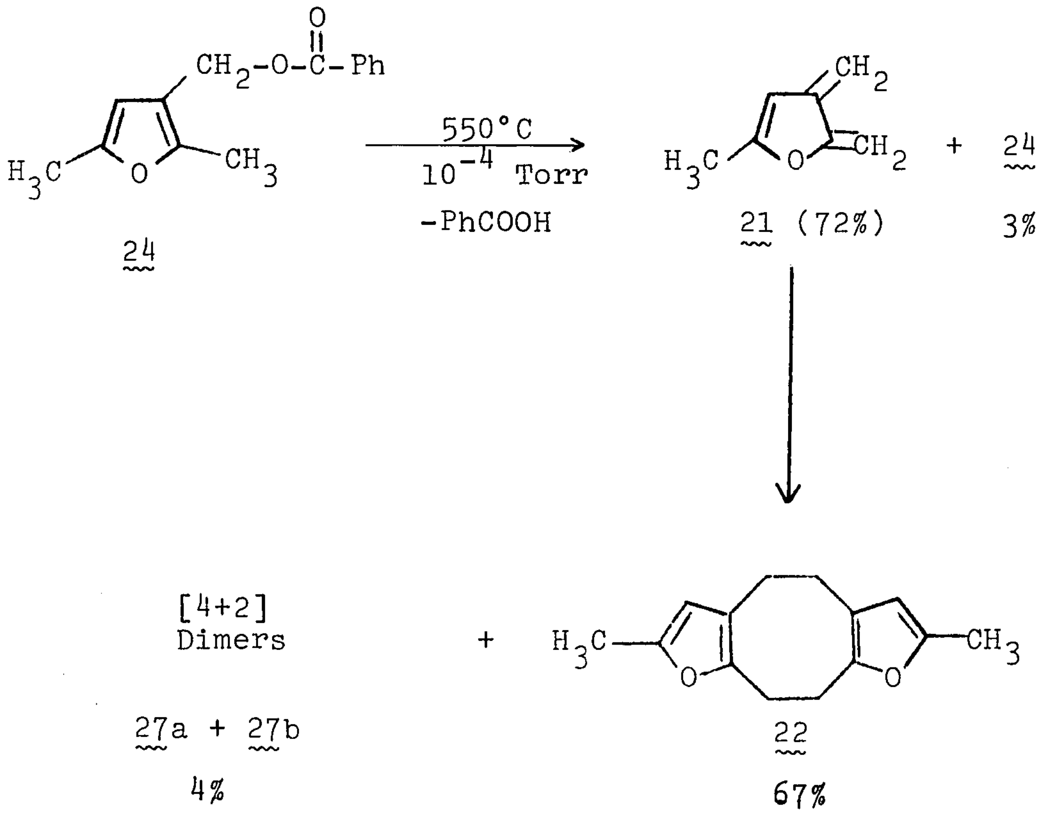
[c] 21 = 5-methyl-2,3-dimethylene-2,3-dihydrofuran.

[d] 22 = [4+4] dimer.

[e] Value not determined.

A maximum yield of 20 was obtained at a pyrolysis temperature of 450°C, while maximum yields of 21 and 22 were obtained for a run at 600°C. In each experiment, there was no firm evidence for a reaction between 20 and 21 when the samples were warmed from -78°C to room temperature. The amounts of 20 and 21 which were lost during the warming process formed a white polymer in the NMR tubes.

A consideration of the mechanism proposed for the conversion of 1 to 2 suggested that the pyrolysis of 2,5-dimethyl-3-furylmethyl benzoate (24) would produce 21 in the absence of 20. Compound (24) was prepared by the lithium aluminum hydride reduction of ethyl 2,5-dimethyl-3-furoate (25)[15] followed by esterification of the resulting 2,5-dimethyl-3-furylmethyl alcohol (26)[11] with benzoyl chloride in the presence of triethylamine. Compound 24 was pyrolyzed at temperatures ranging from 550 to 620°C. No starting ester was recovered at temperatures above 580°C. At each pyrolysis temperature, the only product detected in the samples kept at temperatures below -60°C was 5-methyl-2,3-dimethylene-2,3-dihydrofuran (21). When the samples were warmed to room temperature, 21 dimerized to a mixture consisting mainly of [4+4] dimer 22 along with minor amounts of two [4+2] dimers 27a and 27b.



In Figure 3, the ^1H NMR spectra of the pyrolysis products of **24**, recorded at -60 and 35°C are presented. An interesting feature of the spectra is the absence of peaks corresponding to 5-methylfuranocyclobutene (**28**). The resonance energy of the furan ring in **21** is apparently insufficient to compensate for the strain energy of the four-membered ring. Thus, it appears that the triene **21** is more stable than **28**. This spectral observation is consistent with that observed for 2,3-dimethylene-2,3-dihydrofuran (**12**) and for 4-methyl-2,3-dimethylene-2,3-dihydrofuran (**23**).[7]

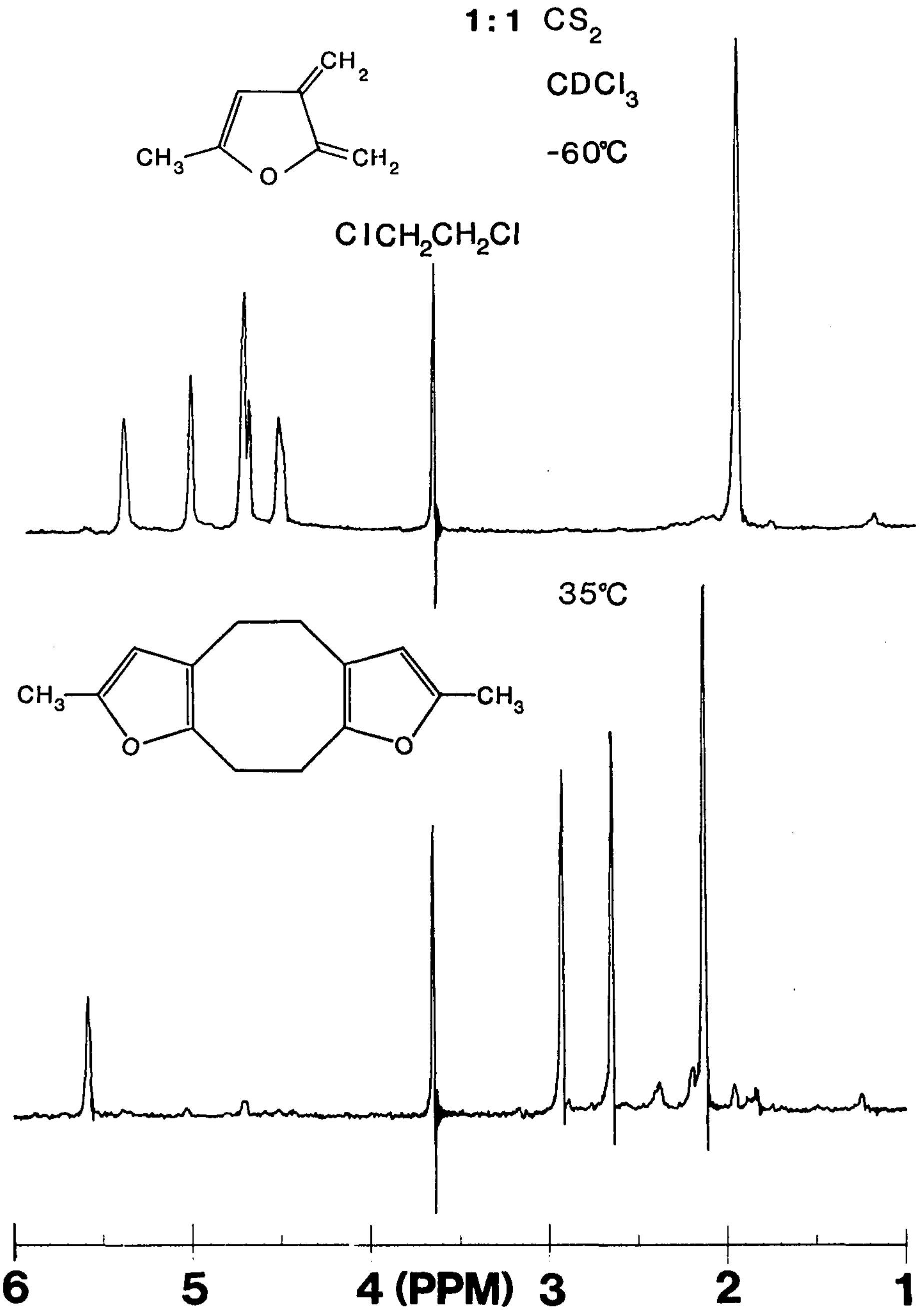
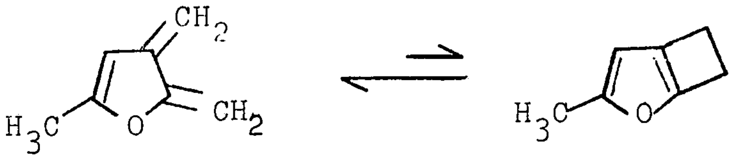


Figure 3. ^{1}H NMR spectra of the pyrolysis products formed from 2,5-dimethyl-3-furylmethyl benzoate (24) recorded at -60°C (top) and at room temperature (bottom).

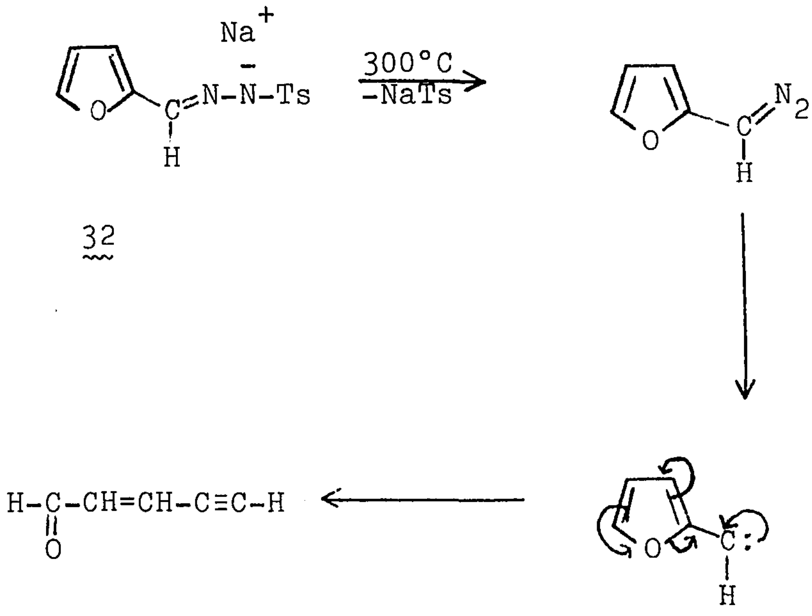


21

28

DISCUSSION

A migration mechanism was previously proposed for the conversion of furfuryl benzoate (**1a**) to methylenecyclobutenone (**2a**).[5] A mechanism which accounts for the formation of the pyrolysis products from 3-methylfurfuryl benzoate (**6**) is presented in Scheme I. The production of **13** can be explained by a direct α elimination of benzoic acid from **6** to form 3-methylfurfurylidine (**29**) followed by ring opening to form **13**. This rearrangement is analogous to the production of *cis*- and *trans*-2-penten-4-ynal (**30**) from furfurylidine (**31**) generated by the pyrolysis of sodium furfuryl tosylhydrazone (**32**).[16]

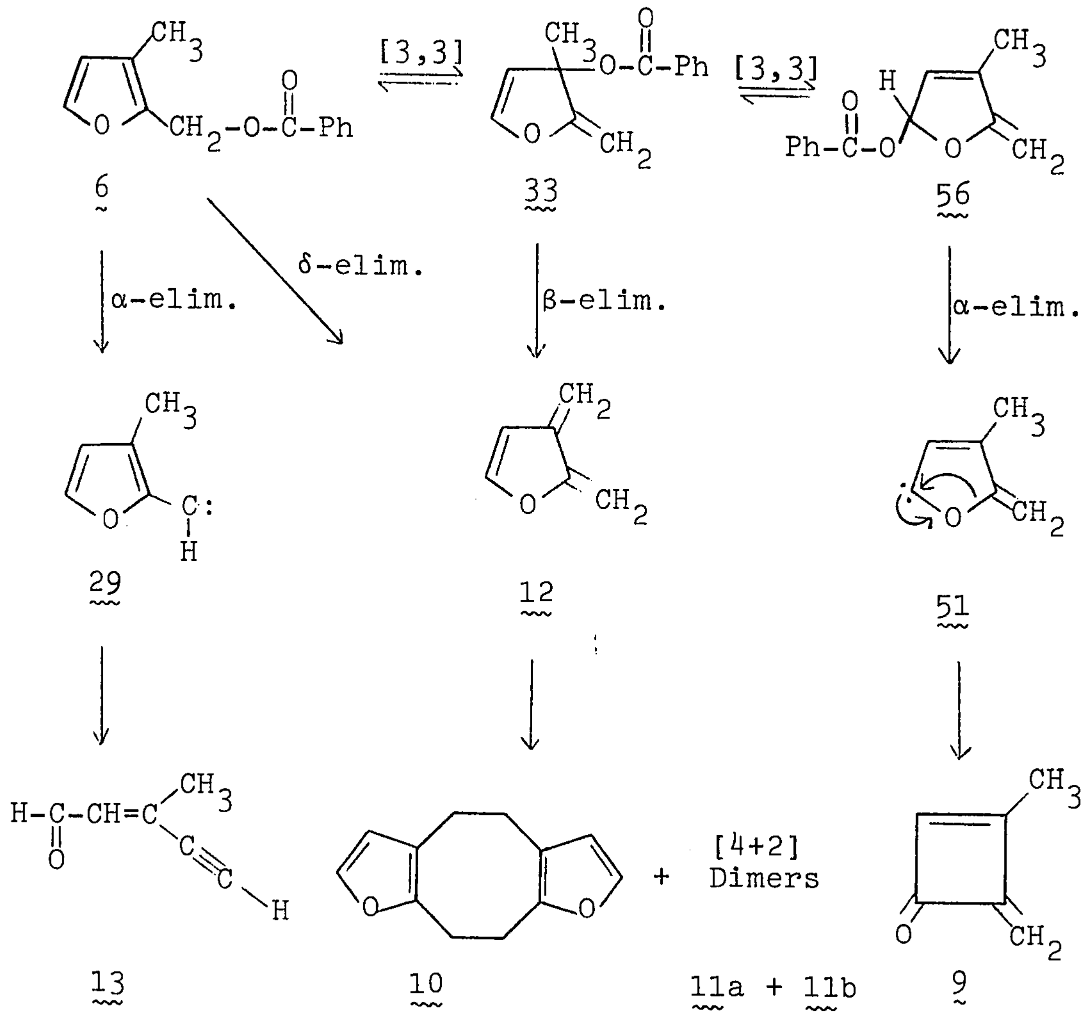


32

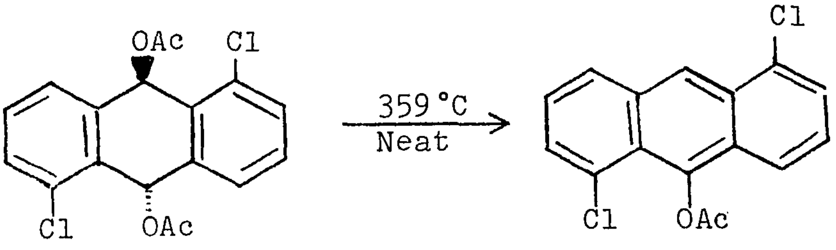
30

31

Scheme I

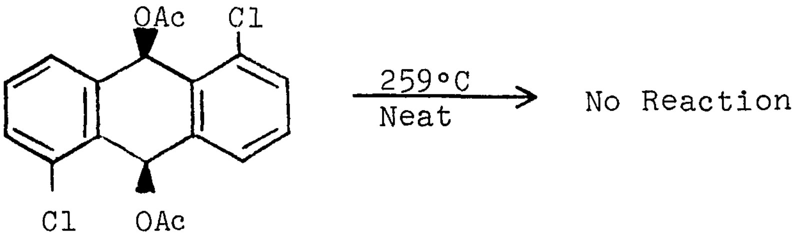


Structure **12** may be formed either directly from **6** by an δ elimination of benzoic acid or by a two-step mechanism involving a [3,3] sigmatropic shift of the benzoate group to form **33**, followed by β elimination of benzoic acid. This 1,4 elimination reaction has literature precedent in the pyrolysis of allylic[17] and benzylic[18] esters containing δ hydrogens. For example, in the pyrolysis of compounds **34** and **35**, the authors concluded that the formation of **36** from **34**, under conditions where **35** is stable, is indicative of a direct δ elimination of acetic acid from **34**.[18c] However, an alternative explanation is that **34** is converted to **36** by a two-step mechanism involving a [3,3] sigmatropic shift of the acetate group followed by β elimination of acetic acid. In **35**, the two-step mechanism is unfavorable because the intermediate ester formed by a [3,3] shift has no hydrogens on the β carbon which will be cis to the acetate group.



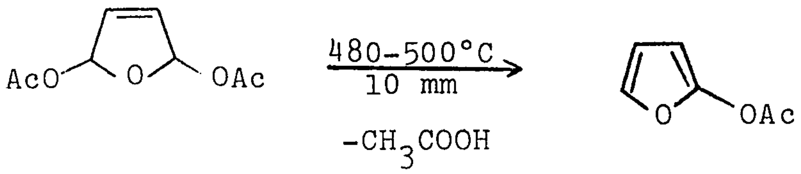
34 **36**

("Good Yield")



35

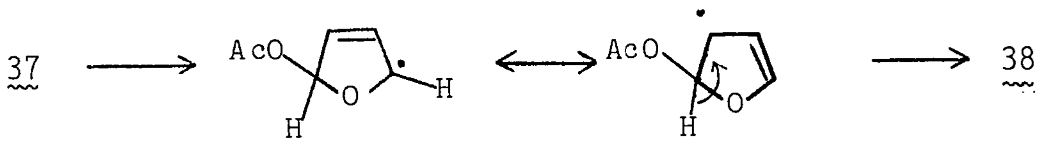
The pyrolysis of either *cis*- or *trans*-2,5-diacetoxy-2,5-dihydrofuran (37) forms 2-acetoxyfuran (38), although in different yields.[17f] Compound 38 may be formed from trans 37



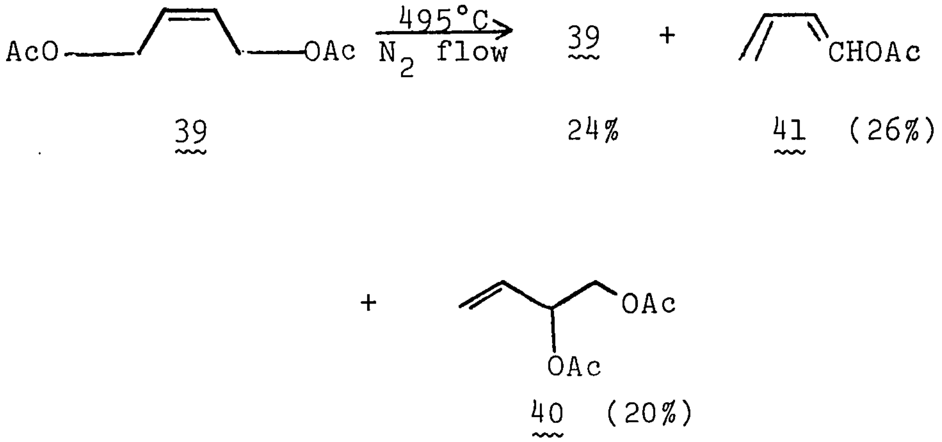
37
cis or trans

38

by either a δ elimination of acetic acid or by a two-step mechanism involving a [3,3] sigmatropic shift of the acetate group followed by β elimination. The conversion of cis 37 to 38 may involve an initial isomerization of cis 37 to trans 37. An alternative route consists of a two-step mechanism involving a [3,3] shift of the acetate group followed by an unfavorable trans elimination of acetic acid. In either cis or trans 37, an initial homolytic cleavage of one of the acetate groups could also lead to 38. None of the isomerized



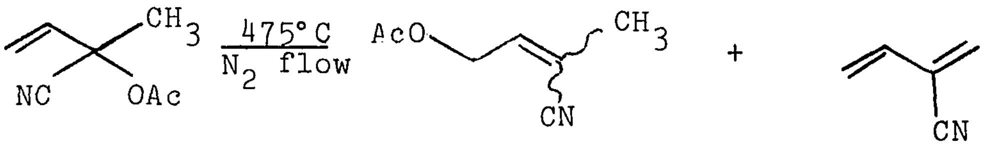
ester formed by a [3,3] sigmatropic shift of the acetate group in 37 was isolated. In the pyrolysis of several allylic systems, the initially formed [3,3] shift products have been isolated.[17a,17e,19] For example, in the pyrolysis of *cis*-1,4-diacetoxy-2-butene (**39**) at 495°C, a 20% yield of 1,2-diacetoxy-3-butene (**40**) was isolated in addition to unreacted, starting material (**39**) (24%) and 1-acetoxy-1,3-butadiene (**41**) (26%).[17a]



39 24% **41** (26%)

40 (20%)

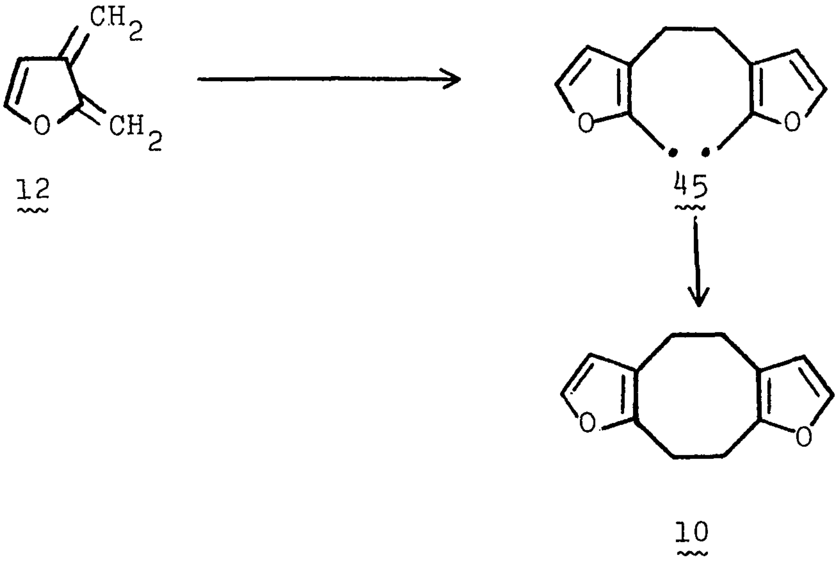
In the pyrolysis of 1-cyano-1-methylallyl acetate (**42**), a 52% yield of 3-cyano-3-methylallyl acetate (**43**) was obtained in addition to 2-cyano-1,3-butadiene (**44**).[19a]

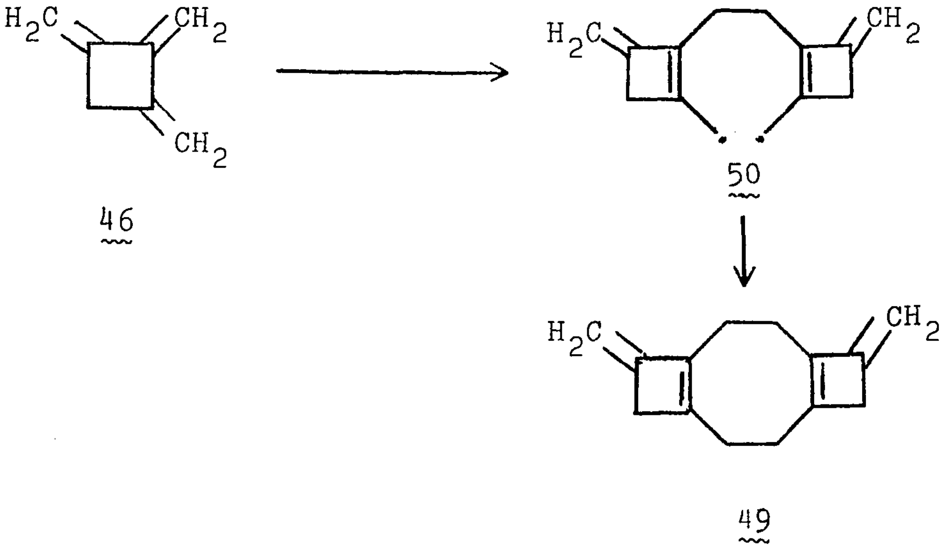


42 **43** **44**

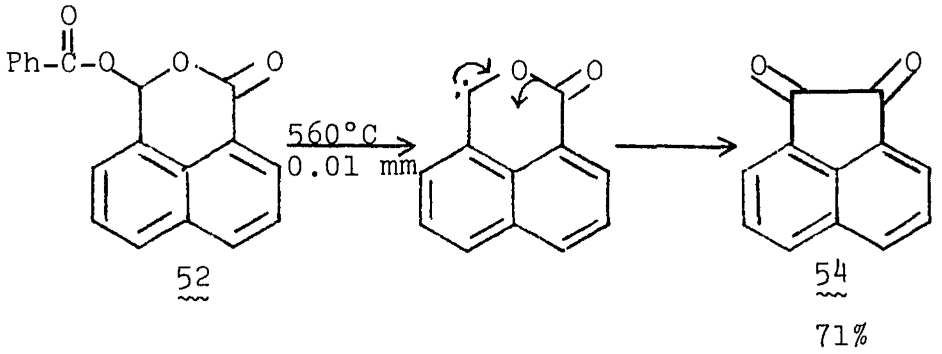
52% 27.6%

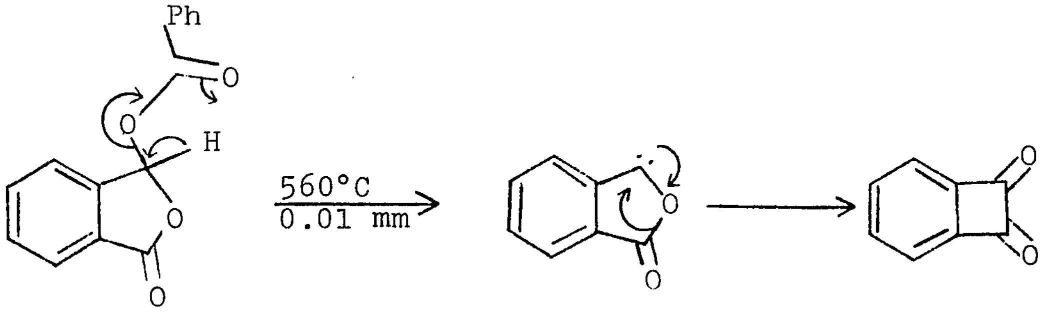
The dimerization of 2,3-dimethylene-2,3-dihydrofuran (**12**) to form predominately the [4+4] dimer **10** has been reported.[7,8a] The mechanism proposed for the conversion of **12** to **10** involves the initial formation of diradical **45** followed by closure to give **10**.[7] This type of dimerization reaction has literature precedent in the reactions of trimethylenecyclobutane (**46**)[20], tetramethylenecyclobutane (**47**)[21] and ortho-xylylene (**48**).[9f] Dimer **49** was the only dimer isolated from **46**[20] and its formation occurs presumedly via diradical intermediate **50**.





The formation of 3-methyl-4-methylene-2-cyclobutenone (9) from 6 can be explained by a multistep mechanism involving two [3,3] sigmatropic shifts of the benzoate group around the furan ring, followed by an α elimination of benzoic acid to form carbene 51. Structure 51 then undergoes a ring contraction to form 9. The conversion of carbene intermediate 51 to 9 has literature precedent in the conversion of benzoyloxylactones 52 and 53 to diones 54 and 55 respectively.[22]



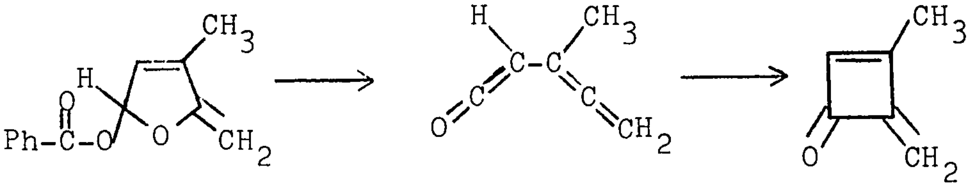


53

55

33%

An alternative mechanism for the formation of 9 involves a concerted elimination of benzoic acid from 56 with concurrent, ring opening to form 3-methyl-2-allenylketene (57), which then undergoes ring closure to form 9.[5-7]



56

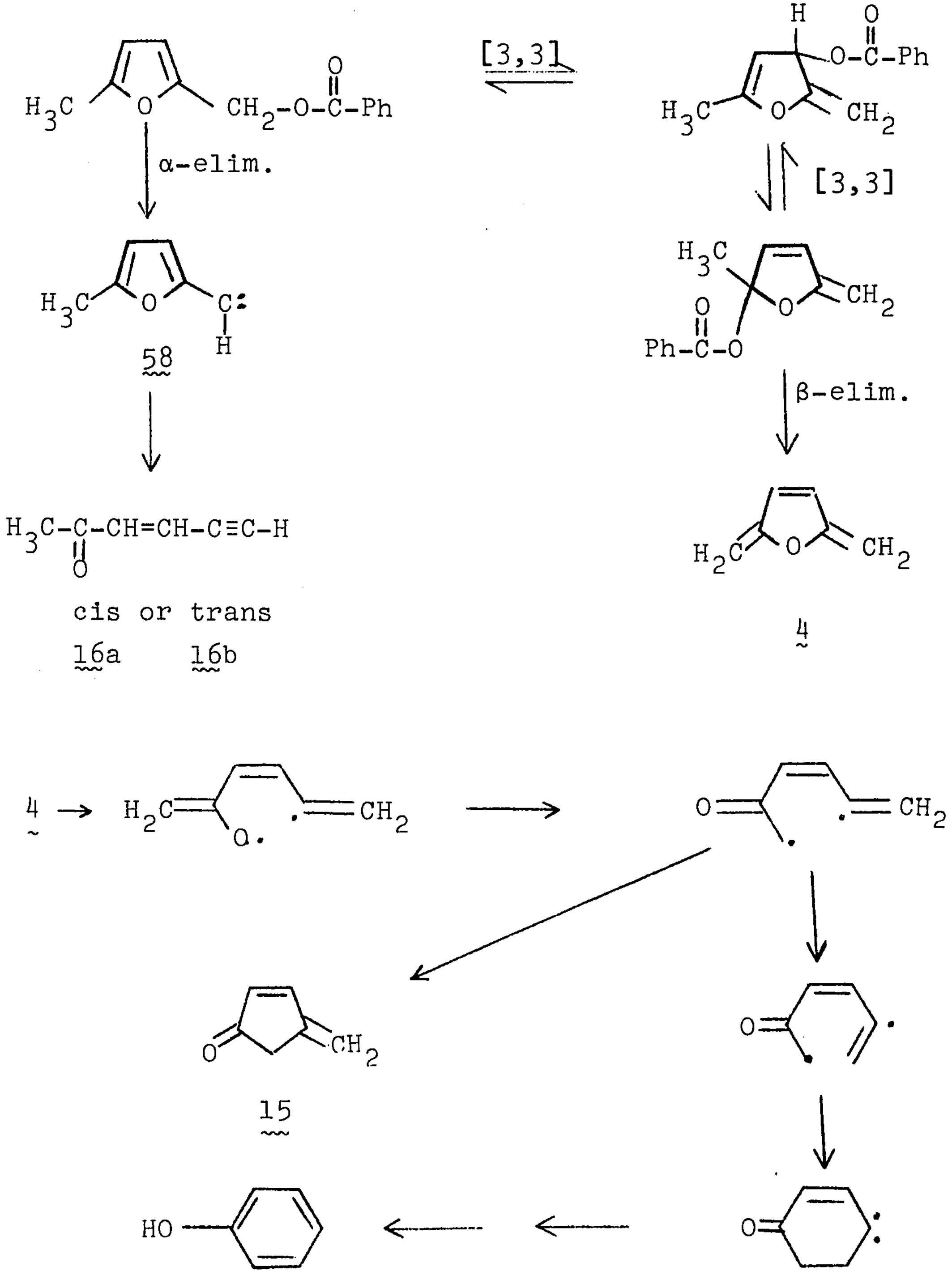
57

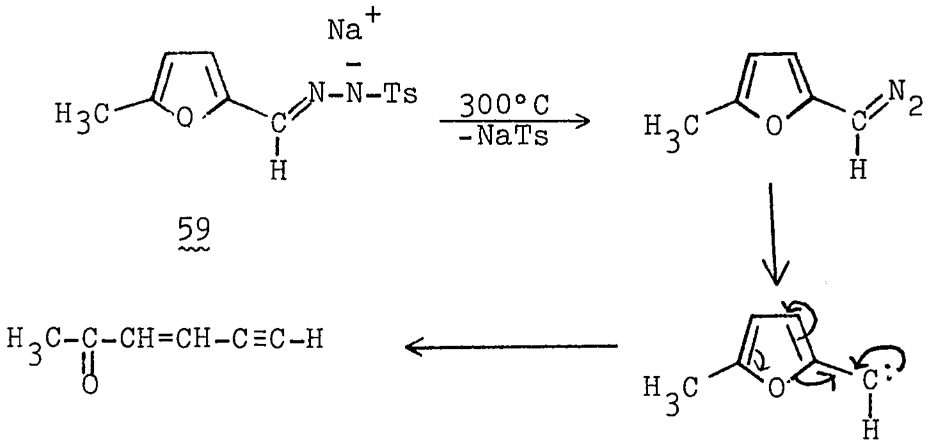
9

The isomerization of allylic esters via [3,3] sigmatropic shifts has been well-documented.[17,19] The formation of compound 9 during the pyrolysis of 6 is remarkable in that an α elimination of benzoic acid occurs in a system containing a site where β elimination can occur. α-Elimination reactions have occasionally been observed in the pyrolysis of esters which can not undergo a β-elimination reaction.[1,5,6,22] Substantial amounts of product 9 were formed during each of the pyrolysis experiments documented in Table I. As the pyrolysis temperature is increased from 450 to 650°C, the ratio of α elimination from the 5 position to β elimination from the 3 position increases. This variation of the elimination ratio with increasing pyrolysis temperature reflects either a change in the relative amounts of intermediates 33 and 56 or a difference in the rates of their respective elimination reactions as the temperature is increased. There have been examples reported of pyrolysis reactions of allylic esters in which β elimination occurs at a rate faster than the rate of allylic isomerization,[17d,17e,23] but this is not a consistently observed phenomenon.[19,24]

In Scheme II, a set of mechanistic pathways which account for the formation of the pyrolysis products from 5-methylfurfuryl benzoate (3) is presented. The formation of trace amounts (<1%) of hex-3-en-5-yn-2-one (16) can be explained by an α elimination of benzoic acid forming 5-methylfurfurylidine (58), followed by ring opening to form either 16a or 16b. The formation of 16a and 16b from a sample of 58 generated by an independent route has been reported.[16]

Scheme II


H3C
CH2-O-C-Ph
O
[3,3]
H
O-C-Ph
CH2
α-elim.
[3,3]
H3C
C:
H
58
Ph-C-O
β-elim.
H3C-C-CH=CH-C≡C-H
O
cis or trans
16a
16b
H2C
CH2
4
4
H2C
O·
CH2
O
CH2
O
CH2
15
O
O
HO



59

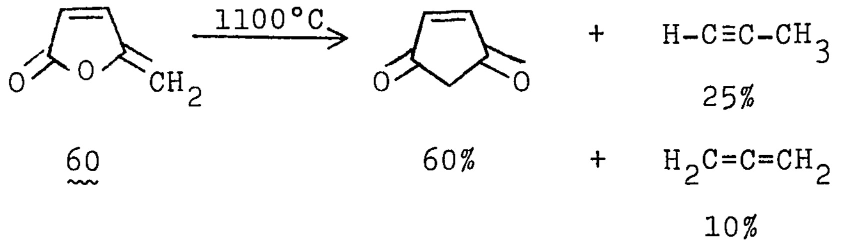
58

cis + trans

16a 16b

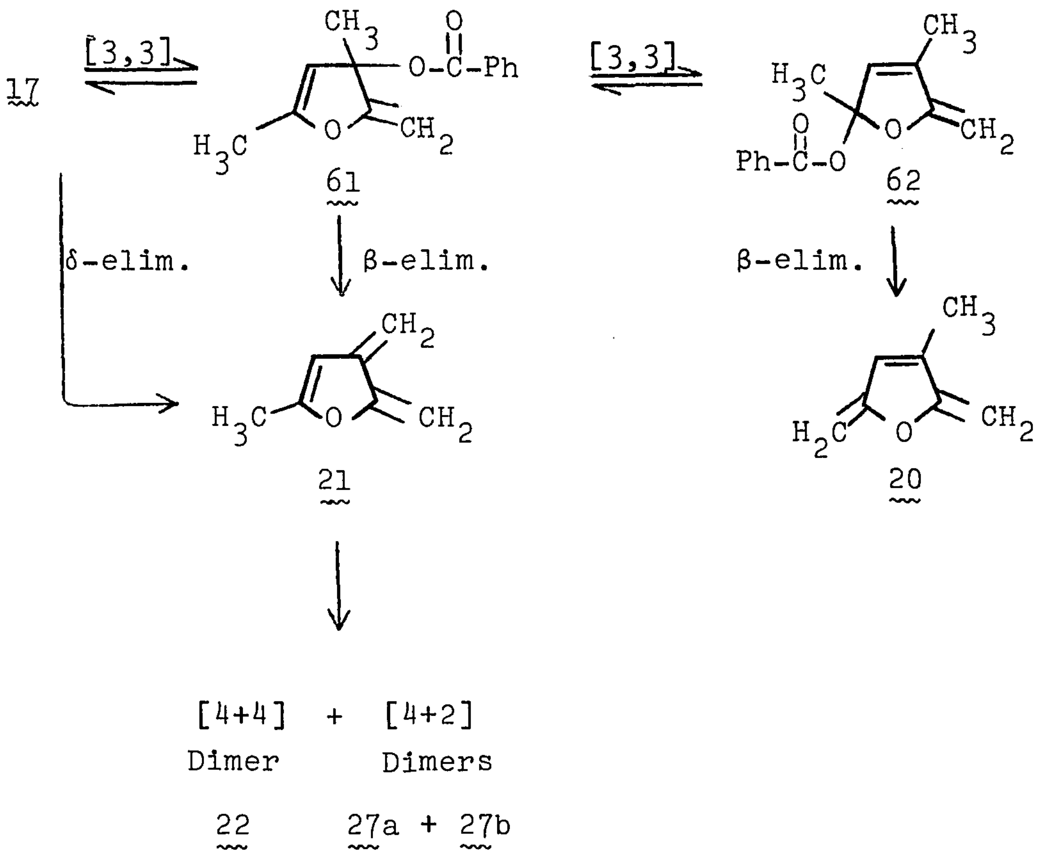
86 : 14 (43%)

The production of 2,5-dimethylene-2,5-dihydrofuran (4) can be explained by a multistep mechanism involving two [3,3] sigmatropic shifts of the benzoate group followed by β elimination of benzoic acid. Compound 4 is the only product formed other than benzoic acid at pyrolysis temperatures between 450 and 550°C. At the higher pyrolysis temperatures, the initial product 4 is converted to a mixture consisting mainly of 4-methylene-2-cyclopentenone (15) and phenol. The conversion of 4 to 15 has literature precedent in the pyrolysis of protoanemonin (60).[25]



Further support for the migration mechanism was obtained from a study of the pyrolysis products of 3,5-dimethylfurfuryl benzoate (17). A set of pathways which account for these products is presented in Scheme III. Structure 21 is formed from 17 either by a direct δ elimination of benzoic acid or by a two-step mechanism involving a [3,3] sigmatropic shift of the benzoate group followed by β elimination of benzoic acid. Product 20 can be explained by a multistep mechanism involving two [3,3] sigmatropic shifts of the benzoate group followed by β elimination of benzoic acid. The ratio of 20 to 21 decreased as the pyrolysis temperature was increased from 400 to 600°C. At temperatures above 600°C, the ratio leveled off to a value of approximately 3.2. The variation of the elimination ratio at the lower pyrolysis temperatures indicates either a change in the relative amounts of intermediates 61 and 62 or a difference in the rates of their respective β eliminations of benzoic acid as the temperature is increased.

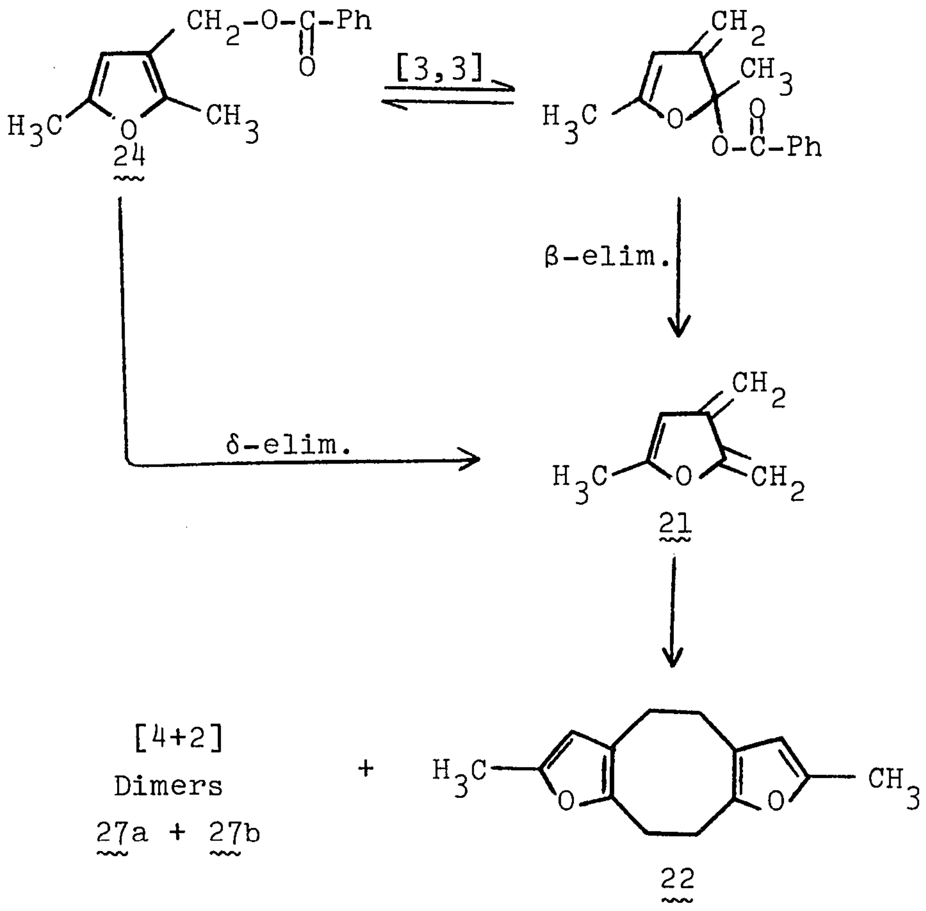
Scheme III



An interesting feature of Tables I, II and III is the difference in the percent conversion for the benzoates 3, 6, and 17 for a given pyrolysis temperature. Complete conversion of 17 is observed at 450°C while 46% of 3 and 15% of 6 are converted under comparable conditions. A general trend observed in ester pyrolysis is that the more acidic the acid produced or the more stable the carbonium ion that would result from alkyl-oxygen cleavage, the faster the reaction.[23,26,27] In the pyrolyses of 3, 6 and 17, the methyl groups serve as electron-donating groups that stabilize the carbonium ions resulting from alkyl-oxygen cleavage in the ester intermediates.

A set of mechanistic pathways which account for the formation of the pyrolysis products from 24 are presented in Scheme IV. Compound 21 is produced from 24 by either a direct δ elimination of benzoic acid or by a two-step mechanism involving a [3,3] sigmatropic shift of the benzoate group, followed by β elimination of benzoic acid. The dimerization of 21 forms predominately the [4+4] dimer 22, along with minor amounts of two [4+2] dimers 27a and 27b. The dimerization products are analogous to those obtained from the dimerization of 2,3-dimethylene-2,3-dihydrofuran (12).

Scheme IV



EXPERIMENTAL

Methods and Materials. The pyrolysis apparatus has been previously described.[28] ^1H NMR spectra were recorded on Varian A-60, EM360, HA-100 or Hitachi-Perkin Elmer R-20B spectrometers. ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer. Chemical shifts are recorded in parts per million (δ) from tetramethylsilane (TMS). Infrared spectra were measured with a Beckman 4250 spectrophotometer. High resolution mass spectra were measured with an Associated Electronics Industries MS-902 instrument at 70 eV. Gas chromatography/mass spectral data (GLC/MS) were recorded using a Finnigan 4000 instrument at 70 eV with an INCOS 2300 data system. GLC analyses were performed using a Hewlett Packard HP 5840 A instrument with a 25 meter, methyl-silicone-coated, capillary column. Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. Elemental analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Acetylacetaldehyde dimethyl acetal, methyl chloroacetate and 5-methylfurfural were obtained from Aldrich Chemical Company. Benzoyl chloride was obtained from Eastman Organic Chemicals. Ethylene glycol and 2,4-pentanedione were obtained from Fisher Scientific Company.

Methyl 3-Methyl-2-furoate (7). Compound 7 was prepared following the procedure of Burness[10] from 132 g (1.0 mole) of acetylacetaldehyde dimethylacetal, 174 g (1.6 mole) of methyl chloroacetate, and 86 g (1.6 mole) of sodium methoxide in 800 mL of dry ether ($LiAlH_4$) at -5°C. After workup, the crude methyl 5,5-dimethoxy-3-methyl-2,3-epoxypentanoate was heated in a simple distillation apparatus until methanol ceased to distil from the reaction mixture at 160°C. The product was then purified by vacuum distillation yielding 78.5 g (0.56 mole; 56%) of 7: mp 33-36°C (lit.[10] mp 34.5-36.5°C); bp 68-72°C (8 mm); IR ($CHCl_3$) 1715, 1600, 1485, 1400, 1292, 1122, 1095, 882, 645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.54 (d, J = 1.5 Hz, 1H), 6.42 (d, J = 1.5 Hz, 1H), 3.89 (s, 3H), 2.33 (s, 3H); high resolution mass spectrum, calcd for $C_7H_8O_3$ 140.04735, measured 140.04740.

3-Methylfurfuryl Alcohol (8). To a stirred slurry of 12.2 g (0.317 mole) of lithium aluminum hydride ($LiAlH_4$) in 150 mL dry ether ($LiAlH_4$) at 0°C was slowly added a solution of 21.12 g (0.151 mole) of methyl 3-methyl-2-furoate (7) in 125 mL dry ether. The mixture was stirred for 1 h at room temperature and then a standard workup[29] gave 16.0 g (0.143 mole; 94.5%) of 8: IR (thin film) 3330, 1500, 1145, 1095, 985, 875 cm^{-1} ^1H NMR ($CDCl_3$) δ 7.2 (d, J = 1.5 Hz, 1H), 6.13 (d, J = 1.5 Hz, 1H), 4.46 (distorted d, J = 5 Hz, 2H), 2.74 (distorted t, J = 5 Hz, 1H), 2.01 (s, 3H); high resolution mass spectrum, calcd for $C_6H_8O_2$ 112.05243, measured 112.05236.

3-Methylfurfuryl Benzoate (6). A solution of 5.43 g (0.039 mole) of benzoyl chloride in 20 mL of dry ether ($LiAlH_4$) was added over a 15 min period to a stirred solution containing 3.73 g (0.033 mole) of 8 and 4.94 g (0.049 mole) of triethylamine in 40 mL dry ether. The mixture was stirred at room temperature for 11 h. After the addition of 15 mL of 5% sodium carbonate, the layers were separated and the aqueous layer was extracted four times with 15 mL of ether. The combined ether layers were washed successively with 1 M hydrochloric acid (3 x 15 mL), saturated sodium bicarbonate (4 x 25 mL) and saturated sodium chloride (2 x 25 mL). After the organic layer was dried (Na_2CO_3), the solvent was removed giving the crude product (7.3 g; quantitative yield) which was purified by vacuum distillation yielding 6.20 g (0.029 mole; 86%) of 6: bp 110°C (0.65 mm); IR (thin film) 1722, 1602, 1583, 1504, 1410, 1265, 1097, 1024, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.22-7.75 (m, 2H), 7.68-7.14 (m, 4H), 6.19 (d, J = 2 Hz, 1H), 5.28 (s, 2H), 2.13 (s, 3H); high resolution mass spectrum, calcd for $C_{13}H_{12}O_3$ 216.07865, measured 216.07803.

5-Methylfurfuryl Alcohol (14).[11] To a stirred slurry of 2.83 g (0.075 mole) of $LiAlH_4$ in 100 mL of dry ether ($LiAlH_4$) at 0°C was slowly added a solution of 16.00 g (0.145 mole) of 5-methylfurfural in 100 mL dry ether. The mixture was stirred at room temperature for 3 h. A standard workup[29] gave 15.78 g (0.14 mole; 97%) of 14: IR (thin film) 3350, 1572, 1225, 1065, 1010, 790, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.17 (d, J = 2.5 Hz, 1H), 5.92 (m, 1H), 4.51 (s, 2H), 2.96 (broad s, 1H), 2.28 (s, 3H); high resolution mass spectrum, calcd for $C_6H_8O_2$ 112.05243, measured 112.05248.

5-Methylfurfuryl Benzoate (3). A solution of 21.54 g (0.153 mole) of benzoyl chloride in 75 mL of dry ether ($LiAlH_4$) was added dropwise over a 20 minute period to a stirred mixture of 15.78 g (0.141 mole) of 14 and 21.63 g (0.214 mole) of triethylamine in 150 mL of dry ether. After stirring the mixture at room temperature for 11 h, 200 mL of 5% sodium carbonate was added and the layers were separated. The aqueous layer was extracted with ether (3 x 50 mL). The combined ether layers were washed successively with 1 M hydrochloric acid (4 x 50 mL), saturated sodium bicarbonate (3 x 50 mL) and saturated sodium chloride (3 x 50 mL). After the organic layer was dried ($MgSO_4$), the solvent was removed giving the crude product. The crude product

(30.93 g; quantitative yield) was purified by vacuum distillation to yield 29.75 g (0.138 mole; 98%) of **3**: bp 97-104°C (0.005 mm); IR (thin film) 1732, 1615, 1595, 1572, 1500, 1275, 1110, 1035, 798 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.28-7.9 (m, 2H), 7.72-7.18 (m, 3H), 6.36 (d, J = 3 Hz, 1H), 5.95 (m, 1H), 5.25 (s, 2H), 2.27 (s, 3H); high resolution mass spectrum, calcd for $C_{13}H_{12}O_3$ 216.07865, measured 216.07824.

*Methyl 3,5-Dimethyl-2-furoate (**18**).* A mixture consisting of 241 g (2.41 mole) of 2,4-pentanedione, 149 g (2.40 mole) of ethylene glycol and 2.5 g (0.013 mole) of *p*-toluenesulfonic acid in 750 mL of benzene was refluxed (bath temperature 110°C) in an apparatus equipped with a Dean and Stark trap for removal of water generated during the reaction. During an 8 h period, 36 mL of water was collected. The solution was cooled, shaken with 5 g of sodium carbonate and then washed successively with saturated potassium bicarbonate (2 x 125 mL) and saturated sodium chloride (2 x 125 mL). The combined aqueous layers were extracted with ether (5 x 100 mL). The combined ether and benzene layers were dried ($MgSO_4$) and the solvents were removed using a rotary evaporater. Distillation of the dark product mixture gave 119.1 g (0.826 mole; 34.3%) of 2,4-pentanedione monoethylene ketal: bp 90-91°C (20 mm) [lit.[11] 31% yield;

bp 49-52°C (3 mm)]; ^{1}H NMR (CCl_4) δ 3.9 (s, 4H), 2.6 (s, 2H), 2.1 (s, 3H), 1.3 (s, 3H). Without further purification, a solution of 119.1 g (0.826 mole) of the ketal and 143.2 g (1.32 mole) of methyl chloroacetate in 800 mL of ether was added dropwise to a stirred suspension of 31.7 g (1.32 mole) of sodium hydride [63.4 g of a 50% dispersion in mineral oil which was washed with pentane (4 x 150 mL)] in 500 mL of ether at 0°C. The mixture was stirred at 0°C for 2 h and then at room temperature for 4 h. After sitting overnight at room temperature, the mixture was again cooled to 0°C and made acidic by the addition of a solution of 10 mL of glacial acetic acid in 150 mL of water. The layers were separated by decanting off the ether layer and the aqueous slurry was extracted with ether (3 x 100 mL). The combined ether layers were washed with 50 mL of a saturated sodium chloride solution to which was added 1 g portions of sodium bicarbonate until the washings were no longer acidic. The ether solution was then washed with saturated sodium chloride (4 x 100 mL), dried ($MgSO_4$) and concentrated. The residue was refluxed in 1 N sulfuric acid (1 L) for 4 h.[30] After cooling the aqueous acid solution, it was extracted with ether (6 x 100 mL), made basic by the slow addition of small portions of sodium carbonate and extracted again with ether (3 x 100 mL). The combined ether layers were washed successively with distilled water (2 x 100 mL), saturated sodium bicarbonate (4 x 75 mL) and saturated sodium chloride (3 x 75 mL). After the organic layer was dried ($MgSO_4$), the solvent was removed giving the crude product which was purified by distillation to give 34.0 g (0.221 mole; 27%) of 18: bp 103-105°C (15 mm) [lit.[11] bp 100-110°C (12 mm)]; IR (thin film) 1720, 1615, 1545, 1402, 1302, 1195, 1165, 1100, 810, 765, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.95 (s, 1H), 3.81 (s, 3H), 2.25 (s, 6H); ^1H NMR (benzene) δ 5.53 (s, 1H), 3.50 (s, 3H), 2.24 (s, 3H), 1.85 (s, 3H), ^{13}C NMR ($CDCl_3$) δ 159.92, 155.53, 138.80, 132.78, 111.92, 51.25, 13.76, 11.54; high resolution mass spectrum, calcd for $C_8H_{10}O_3$ 154.06299, measured 154.06248.

3,5-Dimethylfurfuryl Alcohol (19).[11] To a stirred slurry of 4.45 g (0.1173 mole) of $LiAlH_4$ in 200 mL of dry ether ($LiAlH_4$) at 0°C was added dropwise a solution of 17.94 g (0.116 mole) of 18 in 100 mL of dry ether. The mixture was stirred at room temperature for 4 h and a standard workup[29] gave 13.51 g (0.107 mole; 92%) of 19: IR (thin film) 3360, 1645, 1580, 1400, 1275, 1155, 1115, 995, 915, 795 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.78 (s, 1H), 4.46 (s, 2H), 2.53 (broad s, 1H), 2.21 (s, 3H), 1.97 (s, 3H).

3,5-Dimethylfurfuryl Benzoate (17). A solution of 11.77 g (0.084 mole) of benzoyl chloride in 15 mL of dry ether ($LiAlH_4$) was added dropwise to a stirred solution of 9.55 g (0.076 mole) of 18 and 11.39 g (0.113 mole) of triethylamine in 150 mL of dry ether. After stirring the mixture overnight at room temperature, 25 mL of distilled water was added and the mixture was stirred for 3 h. The layers were separated and the aqueous layer was extracted with ether (2 x 10 mL). The combined ether layers were washed successively with distilled water (3 x 25 mL), 1.5 M hydrochloric acid (3 x 25 mL), saturated sodium bicarbonate (3 x 25 mL) and saturated sodium chloride (2 x 25 mL). After the organic layer was dried ($MgSO_4$), the solvent was removed giving the crude product (15.72 g; 0.068 mole; 90%) which was purified by vacuum distillation yielding 15.18 g (0.066 mole; 87%) of 17: bp 95-101°C (0.005 mm); IR (thin film) 1720, 1600, 1490, 1400, 1265, 1175, 1095, 1020, 920, 795, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.3-8.0 (m, 2H), 7.7-7.2 (m, 3H), 5.84 (broad s with fine splitting, 1H), 5.23 (s, 2H), 2.19 (s, 3H), 2.03 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 166.48, 152.18, 143.35, 132.90, 130.29, 129.75, 128.29, 121.51, 109.38, 57.85, 13.54, 9.91; high resolution mass spectrum, calcd for $C_{14}H_{14}O_3$ 230.09430, measured 230.09366. An analytical sample was purified by sublimation at an oil bath temperature of 52°C (0.5 mm) to yield a white powder: mp 56-57°C.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.11; H, 6.11.

Ethyl 2,5-Dimethyl-3-furoate (25). Sodium metal (11.5 g; 0.5 mole) was slowly added in small pieces, with stirring, to 250 mL of absolute ethanol. After all of the sodium metal was dissolved, the excess ethanol was removed, leaving a white, solid sample of sodium ethoxide. A stirred mixture consisting of the sodium ethoxide, 200 mL of diethyl carbonate and 65.0 g (0.50 mole) of ethyl acetoacetate was heated to 100°C until all of the sodium ethoxide dissolved forming a clear, yellow liquid. After removal of the solvent, the yellow, crude product was washed with diisopropyl ether (10 x 100 mL) yielding the sodium salt of ethyl acetoacetate.[31] Chloroacetone (50.0 g; 0.55 mole) was added dropwise to a stirred solution of the salt and 2.0 g (0.013 mole) of sodium iodide in 200 mL of reagent-grade acetone. The tan mixture was refluxed for 2 h and then stirred at room temperature for 2.5 h. After removal of the acetone by simple distillation, 200 mL of water was added and the layers were separated. The aqueous layer was extracted with ether (6 x 75 mL). The combined ether layers were washed with saturated sodium chloride (3 x 50 mL) and dried ($MgSO_4$). After removal of the solvent, 83.9 g (0.45 mole; 90%) of crude ethyl

2-acetonylacetoacetate was isolated. Upon distillation at 100-105°C (12 mm), the crude product eliminated a molecule of water to form **24**, which was further purified by a second distillation yielding 24.1 g (0.143 mole; 31.8%) of **25**: bp 85-88°C (12 mm) [lit.[15] bp 100-105°C (12 mm)]; IR (thin film) 1715, 1625, 1595, 1405, 1285, 1210, 1085, 1010, 930, 780, cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.26 (broad s, 1H), 4.3 (q, J = 7Hz, 2H), 2.5 (s, 3H), 2.2 (s, 3H), 1.3 (t, J = 7Hz, 3H); high resolution mass spectrum, calcd for $C_9H_{12}O_3$ 168.07865, measured 168.07801.

*2,5-Dimethyl-3-furylmethyl Benzoate (**24**).* To a stirred slurry of 2.43 g (0.064 mole) of $LiAlH_4$ in 100 mL of dry ether ($LiAlH_4$) at 0°C was slowly added a solution of 10.8 g (0.064 mole) of **25** in 100 mL dry ether. After the mixture was stirred for 4 h at room temperature, a standard workup[29] gave 7.57 g (0.060 mole; 94%) of 2,5-dimethyl-3-furylmethyl alcohol (**26**): IR (thin film) 3330, 1635, 1525, 1275, 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.91 (broad s, 1H), 4.32 (s, 2H), 3.15 (s, 1H), 2.19 (s, 6H). Without further purification, compound **26** was converted to benzoate **24**. A solution of 9.3 g (0.066 mole) of benzoyl chloride in 75 mL of dry ether was added dropwise to a stirred solution of 7.57 g (0.060 mole) of **26** and 9.1 g (0.090 mole) of triethylamine in 100 mL dry ether. After stirring the mixture overnight at room temperature, 25 mL of distilled water was added and the mixture was stirred for 2 h. The layers were separated and the aqueous layer was extracted with ether (5 x 10 mL). The combined ether layers were washed successively with 1 M hydrochloric acid (3 x 30 mL), saturated sodium bicarbonate (3 x 25 mL) and saturated sodium chloride (2 x 25 mL). After the organic layer was dried ($MgSO_4$), the solvent was removed yielding the crude product which was purified by column chromatography on silica gel (1% ether in hexanes) followed by distillation, yielding 12.1 g (0.053 mole; 88%) of **24**: bp 112°C (0.8 mm); IR (thin film) 1725, 1645, 1590, 1495, 1400, 1275, 1175, 1155, 1105, 1030, 880 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.2-7.8 (m, 2H), 7.7-7.2 (m, 3H), 5.98 (s, 1H), 5.12 (s, 2H), 2.34 (s, 3H), 2.25 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 166.3, 149.9, 148.8, 132.6, 130.5, 129.5, 128.1, 115.2, 107.3, 58.6, 13.1, 11.3; high resolution mass spectrum, calcd for $C_{14}H_{14}O_3$ 230.09430, measured 230.09434.

General Pyrolysis Procedure. The pyrolyses were run at furnace temperatures from 400 to 800°C. A sample of the furylmethyl ester in a Pyrex boat was placed into the sample compartment and the apparatus was evacuated to ca. 10^{-4} Torr. The sample chamber was heated to ca. 75°C. A condenser cooled to ca. -20°C was inserted between the furnace and the liquid-nitrogen-cooled trap to collect the unreacted starting material and the benzoic acid formed as a biproduct. During the pyrolysis, 2 mL of a 1:1 mixture of carbon disulfide (CS_2) and deuterochloroform ($CDCl_3$) was deposited onto the trap through a side arm. After all of the starting material was gone from the sample compartment, nitrogen was introduced into the system and a known amount of dichloroethane standard was added. The trap was then warmed to -78°C and a 1:1 mixture of CS_2 and $CDCl_3$ (2 mL) was used to rinse the material on the insert to the bottom of the trap. The product solution was mixed by rinsing the walls of the trap with the solution ca. ten times using a cold pipette (CS_2 at -78°C). Most of the product solution was placed into four 5 mm, NMR tubes at -78°C and NMR spectral data was recorded at temperatures below -60°C for each tube. The tubes were then warmed to room temperature and NMR spectra were recorded. The remainder of the product solution was used for GLC analysis.

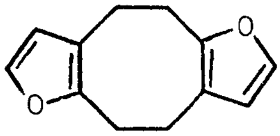
Pyrolysis of 3-Methylfurfuryl Benzoate (6).[7] Pyrolyses were carried out with ca. 0.31 g of 6 at 450, 550, 650, and 750°C using the general procedure. After the product solution was placed into the NMR tubes at -78°C, the tubes were slowly warmed to room temperature and NMR spectra were recorded. The yields of recovered starting material 6, as well as products 9 and 10, were determined by quantitative ^{1}H NMR analysis using known amounts of dichloroethane as an internal standard. Yields of the minor products 11a, 11b and 13 were determined by GLC analysis using a 25 m, methyl-silicone-coated, capillary column (column temperature 50°C for 10 minutes followed by temperature programming at a rate of 5°C per minute until a temperature of 150°C was reached). Yields of the pyrolysis products from 6 are presented in Table I. The products were identified from the following data.

3-Methyl-4-methylene-2-cyclobutenone (9): IR (1:1 $CS_2/CDCl_3$) 1780 cm^{-1}; ^{1}H NMR (1:1 $CS_2/CDCl_3$) δ 6.8 (m, 1H), 5.02 (m, 1H), 4.66 (m, 1H), 2.3 (d, J = 1.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 187.68, 186.18, 159,65, 149.70, 95.34, 13.98; GLC/MS (70 eV) m/e (relative intensity) 96.10 (0.32), 95.10 (5.59), 94.02 (100.00), 66.04 (84.99), 64.98 (65.20), 63.04 (13.45), 54.02 (12.13), 51.04 (38.89), 50.04 (27.58).

4H,5H,9H,10H-Cycloocta[1,2-b:6,5-b']difuran (10): mp 52-53°C (lit.[8a] mp 54-55°C); IR (1:1 $CS_2/CDCl_3$) 1600, 1505, 1425, 1040, 895, 735 cm^{-1}; ^{1}H NMR (1:1 $CS_2/CDCl_3$) δ 7.09 (d, J = 2 Hz, 2H), 6.0 (d, J = 2 Hz, 2H), 3.03 (s, 4H), 2.76 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 149.9 (s), 139.7 (d, J = 200 Hz), 117.9 (s), 113.4 (d, J = 172 Hz), 25.8 (t, J = 126 Hz), 24.9

(t, J = 128 Hz); GLC/MS m/e (relative intensity) 190.08 (0.33), 189.08 (3.74), 188.08 (29.19), 173.02 (11.21), 159.08 (5.20), 146.06 (3.89), 145.04 (9.03), 131.06 (6.66), 115.04 (3.57), 95.06 (8.51), 94.02 (100.00), 91.06 (4.09), 77.02 (7.41), 66.04 (17.83), 65.04 (12.34), 63.04 (3.70), 54.92 (6.46), 53.04 (4.66), 52.06 (4.16), 51.02 (10.12); high resolution mass spectrum, calcd for $C_{12}H_{12}O_2$ 188.08373, measured 188.08359.

[4+2] Dimers **11a** and **11b**: ^{1}H NMR (1:1 $CS_2/CDCl_3$) (small peaks observed in a spectrum of the product mixture) δ 7.09 (2H), 6.0 (2H), 4.76 (m, 1H), 4.47 (m, 1H), 2.56-2.23 (m, 4H), 1.9 (m, 1H); GLC/MS (isomer a) m/e (relative intensity) 190.06 (0.06), 189.06 (2.15), 188.06 (17.11), 173.04 (8.96), 159.06 (4.14), 145.04 (6.86), 131.02 (5.31), 115.04 (3.41), 95.04 (6.70), 94.00 (100.00), 91.06 (4.08), 77.02 (5.40), 66.04 (13.84), 65.02 (9.29), 51.02 (7.41); GLC/MS (isomer b) m/e (relative intensity) 190.04 (0.02), 189.06 (2.95), 188.08 (25.87), 173.04 (11.93), 159.08 (4.87), 145.04 (9.87), 131.04 (6.59), 115.06 (4.22), 95.04 (6.95), 94.02 (100.00), 91.06 (12.08), 77.02 (5.17), 66.02 (10.93), 65.02 (10.04), 54.94 (6.16), 51.02 (8.73). It should be noted that while the GLC/MS data does not rule out the possibility that one of the minor dimers **11a** or **11b** is the head-to-tail, [4+4] dimer 63, the absence of ^{1}H NMR and ^{13}C NMR signals corresponding to 63 makes it unlikely.



63

3-Methyl-2-penten-4-ynal 13a or 13b: GLC/MS m/e (relative intensity) 97.00 (0.31), 95.00 (1.53), 94.00 (44.95), 93.00 (10.78), 79.00 (2.37), 67.00 (5.50), 66.00 (100.00), 65.00 (72.09), 63.00 (22.40), 62.00 (14.68), 61.00 (5.81), 51.00 (29.13), 50.00 (29.43), 49.00 (7.72).

Pyrolysis of 5-Methylfurfuryl Benzoate (3). Pyrolyses were carried out at 450, 550, 650, 750 and 850°C using the general procedure and ca. 0.3 g of 3 in each experiment. After the samples were warmed to room temperature, the yields of recovered starting material 3 and product 4 were determined by quantitative ^{1}H NMR analysis using a dichloroethane standard. The yields of products 15,16 and phenol were determined by GLC analysis (same temperature program as that used for analysis of the products from 6). Yields of the pyrolysis products from 3 are presented in Table II. The products were identified from the following data.

*2,5-Dimethylene-2,5-dihydrofuran (**4**)*^{5,8a}: ^{1}H NMR (1:1 $CS_2/CDCl_3$) δ 6.42 (s, 2H), 4.52 (d, J = 1.5 Hz, 2H), 4.22 (d, J = 1.5 Hz, 2H); ^{13}C NMR (1:1 $CS_2/CDCl_3$) 162.09, 128.50, 84.35; GLC/MS m/e (relative intensity) 96.06 (0.48), 95.08 (6.95), 94.04 (100.00), 66.06 (22.98), 65.00 (29.84), 54.94 (8.64), 52.06 (5.48), 51.04 (17.89), 50.02 (16.28), 47.06 (10.59).

*4-Methylene-2-cyclopentenone (**15**)*: IR (1:1 $CS_2/CDCl_3$) 1705 cm^{-1}; ^{1}H NMR (1:1 $CS_2/CDCl_3$) δ 7.7 (d of m, J = 6 Hz, 1H), 6.28 (d of m, J = 6 Hz, 1H), 5.39 (m, 1H), 5.28 (m, 1H), 2.95 (m, 2H); ^{13}C NMR (1:1 $CS_2/CDCl_3$) δ 207.8, 160.2, 143.8, 135.1, 114.7, 41.62; GLC/MS m/e (relative intensity) 96.06 (0.36), 95.04 (6.24), 94.00 (100.00), 67.06 (4.28), 66.04 (79.75), 64.98 (46.73), 63.02 (7.85), 62.02 (4.63), 55.00 (16.36), 51.02 (11.10), 50.02 (10.59).

*cis- or trans-hex-3-en-5-yn-2-one (**16a** or **16b**)*: GLC/MS m/e (relative intensity) 96.62 (0.21), 95.04 (1.90), 94.04 (43.73), 80.06 (4.23), 78.98 (100.00), 66.12 (1.13), 63.06 (1.06), 52.08 (2.89), 51.02 (64.72), 50.04, (30.70), 49.02 (5.63).

Phenol: IR (1:1 $CS_2/CDCl_3$) 3330 cm^{-1}; ^{1}H NMR (1:1 $CS_2/CDCl_3$) δ 7.25-6.55 (m, 5H); ^{13}C NMR (1:1 $CS_2/CDCl_3$) δ 129.41, 119.66, 114.97 (carbons 3,5; 4 and 2,6 respectively:

a peak for carbon-1 at δ 155.0 was not present in the spectrum); GLC retention time and GLC/MS data matched that of an authentic sample of phenol; GLC/MS m/e (relative intensity) 96.02 (0.37), 95.04 (6.69), 94.00 (100.00), 66.02 (33.31), 65.02 (28.04), 63.00 (7.16), 54.98 (10.21), 51.02 (6.55), 50.00 (7.42), 46.94 (6.51).

Pyrolysis of 3,5-Dimethylfurfuryl Benzoate (17). Pyrolyses of 17 were carried out at 400, 450, 500, 600 and 700°C using the general procedure. Yields of products from 17 were determined by quantitiative ^{1}H NMR analysis employing dichloroethane as a standard and are presented in Table III. Product yields were determined initially at -60°C and again after warming the samples slowly to room temperature. The products were identified from the following data.

3-Methyl-2,5-dimethylene-2,5-dihydrofuran (20): ^{1}H NMR (1:1 $CS_2/CDCl_3$) δ 6.18 (m, 1H), 4.44 (m, 2H), 4.14 (m, 2H), 1.95 (distorted d with fine splitting, J = 1.0 Hz, 3H); ^{13}C NMR (1:1 $CS_2/CDCl_3$) δ 163.3, 161.0, 137.7, 125.1, 82.6, 81.4, 11.0.

5-Methyl-2,3-dimethylene-2,3-dihydrofuran (21): ^{1}H NMR (1:1 $CS_2/CDCl_3$) δ 5.46 (m, 1H), 5.07 (m, 1H), 4.76 (m, 2H), 4.57 (m, 1H), 2.01 (broad s with fine splitting, 3H).

2,7-Dimethyl-4H,5H,9H,10H-cycloocta[1,2-b:6,5-b']difuran (22): IR (thin film) 1610, 1575, 1065, 940, 885, 790, 747 cm^{-1}; ^1H NMR (1:1 $CS_2/CDCl_3$) δ 5.60 (m, 2H), 2.94 (s, 4H), 2.66 (s, 4H), 2.15 (m, 6H); ^{13}C NMR (1:1 $CS_2/CDCl_3$) δ 149.03, 148.00, 118.64, 109.38, 25.95, 24.97, 13.33; an analytical sample of 22 was prepared by removal of the solvent and subliming the residue at a bath temperature of 60°C (0.05 mm): mp 61-63°C; high resolution mass spectrum, calcd for $C_{14}H_{16}O_2$ 216.11503, measured 216.11486.

Pyrolysis of 2,5-Dimethyl-3-furylmethyl Benzoate (24). A 0.3171 g (1.4 mmol) quantity of 24 was pyrolyzed at 550°C using the general procedure. A ^1H NMR spectrum of the pyrolysate recorded at -60°C, indicated that 5-methyl-2,3-dimethylene-2,3-dihydrofuran (21) was the only major product: ^1H NMR (1:1 $CS_2/CDCl_3$; -60°C) δ 5.44 (m, 1H), 5.05 (m, 1H), 4.75 (m, 2H), 4.55 (m, 1H), 2.01 (broad s with fine splitting, 3H). Quantitative ^1H NMR analysis indicated that 0.930 mmol of 21 (68%) was present in the NMR tubes. Upon warming the samples to room temperature, 21 dimerized cleanly to a mixture consisting mainly of [4+4] dimer 22 along with smaller amounts of two [4+2] dimers 27a and 27b. ^1H NMR analysis using a dichloroethane standard indicated that a quantitative yield of dimers 22, 27a and 27b was formed from 21. GLC analysis indicated that the relative amounts of the dimers were 93.6% of [4+4] dimer 22 and 5.4% of two [4+2] dimers 27a and 27b (8:1 ratio). In addition to the pyrolysis products, 2.7% of the starting ester was recovered.

Preparative Scale Pyrolysis of 24. A 1.6112 g (7.0 mole) quantity of 24 was pyrolyzed at 610°C. During the pyrolysis, 10 mL of carbon disulfide was deposited onto the trap via a side arm. After the apparatus was shut down under nitrogen, the trap was warmed to -78°C and 10 mL of carbon disulfide was used to rinse the material on the insert to the bottom of the trap. After 30 min at -78°C, the trap was immersed in an ice bath and maintained at 0°C for 10 h. The product solution was then warmed to room temperature, dried (Na_2CO_3) and concentrated, yielding 1.3317 g (6.16 mmol; 87%), of a pale-yellow oil. Crystallization from freshly-distilled, Skelly B yielded 0.9685 g (4.5 mmol; 64%) of fluffy, white needles of 22: mp 64°C; IR ($CHCl_3$) 1605, 1570, 1062, 895, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.67 (m, 1H), 3.02 (s, 4H), 2.73 (s, 4H), 2.17 (broad s with fine splitting, 6H); ^{13}C NMR (1:1 $CS_2/CDCl_3$) δ 148.7, 147.8, 118.6, 109.4, 26.0, 25.1, 13.3; high resolution mass spectrum, calcd for $C_{14}H_{16}O_2$ 216.11503, measured 216.11477.

REFERENCES

1. Trahanovsky, W. S.; Park, M.-G. J. Am. Chem. Soc. 1973, 95, 5412.

2. DeSelms, R. C.; Delay, F. J. Am. Chem. Soc. 1973, 95, 274.

3. Cava, M. P. "Cyclobutadiene and Related Compounds"; Academic Press: New York, 1967; p 157-158.

4. For alternate routes to cyclobutane derivatives see:

   a) Brady, W. T.; Stockton, J. D.; Patel, A. D. J. Org. Chem. 1974, 39, 236.

   b) Bampfield, H. A.; Brook, P. R.; Hunt, K. Chem. Commun. 1976, 146.

   c) Spangler, R. J.; Kim, J. H.; Cava, M. P. J. Org. Chem. 1977, 42, 1697.

   d) Snider, B. B.; Brown, L. A.; Eichen Conn, R. S.; Killinger, T. A. Tetrahedron Lett. 1977, 2831.

   e) Trost, B. M.; Scudder, P. H. J. Am. Chem. Soc. 1977, 99, 7601.

5. Trahanovsky, W. S.; Park, M.-G. J. Org. Chem. 1974, 39, 1448.

6. Trahanovsky, W. S.; Alexander, D. L. J. Am. Chem. Soc. 1979, 101, 142.

7. Trahanovsky, W. S.; Cassady, T. J.; Woods, T. L. J. Am. Chem. Soc. 1981, 103, 6691.

8. For alternate syntheses of dimethylenedihydrofurans see:

   a) Winberg, H. E.; Fawcett, F. S.; Mochel, W. E.; Theobald, C. W. J. Am. Chem. Soc. 1960, 82, 1428.

   b) Jullien, J.; Pechine, J. M.; Perez, F.; Piade, J. J. Tetrahedron Lett. 1979, 3079.

9. a) Mc Cullough, J. J. Acc. Chem. Res. 1980, 13, 270.

b) Flynn, C. R.; Michl, J. J. Am. Chem. Soc. 1974, 96, 3280.

c) Migirdicyan, E.; Baudet, J. J. Am. Chem. Soc. 1975, 97, 7400.

d) Tseng, K. L.; Michl, J. J. Am. Chem. Soc. 1977, 99, 4840.

e) Steiner, R. P.; Miller, R. D.; Dewey, H. J.; Michl, J. J. Am. Chem. Soc. 1979, 101, 1820.

f) Errede, L. A. J. Am. Chem. Soc. 1961, 83, 949.

10. Burness, D. M. "Organic Syntheses", Collect. Vol. IV; Wiley: New York, 1963; p 649.

11. Elliot, M; Janes, N. F.; Pearson, B. C. Pestic. Sci. 1971, 2, 243.

12. Pouchert, C. J.; Campbell, J. R. "The Aldrich Library of ^{1}H NMR Spectra"; The Aldrich Chemical Co. Inc.: Milwaukee, 1974; Vol. I, p 139A.

13. Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; p 193.

14. Pouchert, C. "The Aldrich Library of Infrared Spectra", 2nd ed.; Aldrich Chemical Co. Inc.: Milwaukee, 1975; Vol. I, p 235F.

15. Dann, O.; Distler, H.; Merkel, H. Chem. Ber. 1952, 85, 457.

16. Hoffman, R. V.; Orphanides, G. G.; Shechter, H. J. Am. Chem. Soc. 1978, 100, 7927.

17. a) Bailey, W. J.; Barclay, R., Jr. J. Org. Chem. 1956, 21, 328.

b) Grummitt, O.; Splitter, J. J. Am. Chem. Soc. 1952, 74, 3924.

c) Grummitt, O.; Mandel, Z. J. Am. Chem. Soc. 1956, 78, 1054.

d) Bailey, W. J.; Goossens, J. C. *J. Am. Chem. Soc.* 1956, 78, 2804.

e) Greenwood, F. L. *J. Org. Chem.* 1959, 24, 1735; 1962, 27, 2308.

f) Clauson-Kaas, N.; Elming, N. *Acta Chem. Scand.* 1952, 6, 560.

18. a) Trahanovsky, W. S.; Morello, M. J. "Abstracts of Papers", 178th National Meeting of the American Chemical Society, Washington, D.C., Sept. 1979; American Chemical Society: Washington, D.C., 1979; PETR 46.

b) Morello, M. J. M.S. Thesis, Iowa State University, Ames, Iowa, 1980.

c) Cristol, S. J.; Barasch, W.; Tieman, C. H. *J. Am. Chem. Soc.* 1955, 77, 583.

19. a) Marvell, C. S.; Brace, N. O. *J. Am. Chem. Soc.* 1948, 70, 1775.

b) Landor, P. D.; Landor, S. R. *J. Chem. Soc.* 1956, 1015.

c) Heilbron, I. M.; Jones, E. R. H.; Mc Combie, J. T.; Weedon, B. C. *J. Chem. Soc.* 1945, 88.

d) Burton, H. *J. Chem. Soc.* 1928, 1650.

e) Balfe, M. P.; Kenyon, J. *Trans. Faraday Soc.* 1941, 37, 721.

f) Braude, E. A.; Turner, D. W.; Waight, E. S. *J. Chem. Soc.* 1958, 2396.

g) Braude, E. A.; Turner, D. W. *J. Chem. Soc.* 1958, 2404.

20. Martin, H.-D.; Mayer, B. *Tetrahedron Lett.* 1979, 2351.

21. Griffin, G. W.; Peterson, L. I. *J. Am. Chem. Soc.* 1963, 85, 2268.

22. a) Kwart, H.; Hoster, D. P. *Chem. Commun.* 1967, 1155.

    b) Kwart, H.; Ling, H. G. *Chem. Commun.* 1969, 302.

    c) Lehr, R. E.; Wilson, J. M. *Chem. Commun.* 1971, 666.

    d) Hoffmann, R. W.; Schuttler, R.; Loof, I. H. *Chem. Ber.* 1977, 110, 3410.

    e) Oele, P. C.; Louw, R. *Tetrahedron Lett.* 1972, 4941.

    f) Brown, R. F. C.; Eastwood, F. W.; Lim, S. T.; McMullen, G. L. *Aust. J. Chem.* 1976, 29, 1705.

23. Smith, G. G.; Kelley, F. W. In "Progress in Physical Organic Chemistry"; Streitwieser, A.; Taft, R. W., Eds.; Wiley: New York, 1971; Vol. VIII, Chapter 2.

24. Lewis, E. S.; Hill, J. T.; Newman, E. R. *J. Am. Chem. Soc.* 1968, 90, 662.

25. Bloch, R.; Orvane, P. *Tetrahedron Lett.* 1981, 22, 3597.

26. DePuy, C. H.; King, R. W. *Chem. Rev.* 1960, 60, 431.

27. Wertz, D. H.; Allinger, N. L. *J. Org. Chem.* 1977, 42, 698.

28. Trahanovsky, W. S.; Ong, C. C.; Pataky, J. G.; Weitl, F. L.; Mullen, P. W.; Clardy, J. C.; Hansen, R. S. *J. Org. Chem.* 1971, 36, 3575.

29. Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. I, p 584.

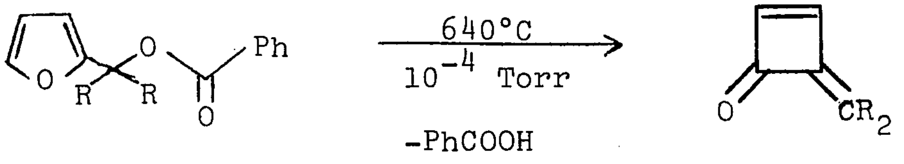
30. Cornforth, J. W. *J. Chem. Soc.* 1958, 1310.

31. Wallingford, V. A.; Homeyer, A. H. U.S. Patent 2,391,530 (1945); *Chem. Abstracts* 1946, 40, 3771^1.

SECTION IV. FORMATION OF VINYLACETYLENE AND METHYLENECYCLOBUTENONE BY THE FLASH VACUUM PYROLYSIS OF 3-FURYLMETHYL BENZOATE

INTRODUCTION

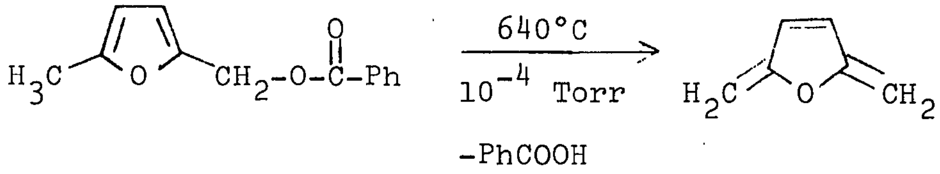
The flash vacuum pyrolysis (FVP) of furfuryl benzoate (1a) gives a moderate yield of methylenecyclobutenone (2a) along with benzoic acid and some minor products.[1] This reaction makes available the parent compound of a series of compounds which is not easily synthesized.[2] Methylenecyclobutenone (1a) was, prior to that report, one of the missing cyclobutadiene derivatives[3] and is a potentially useful synthetic intermediate since it has a highly functionalized, cyclobutane moiety.[4]



1a, R=H
40%
2a, R=H

1b, R=D
2b, R=D

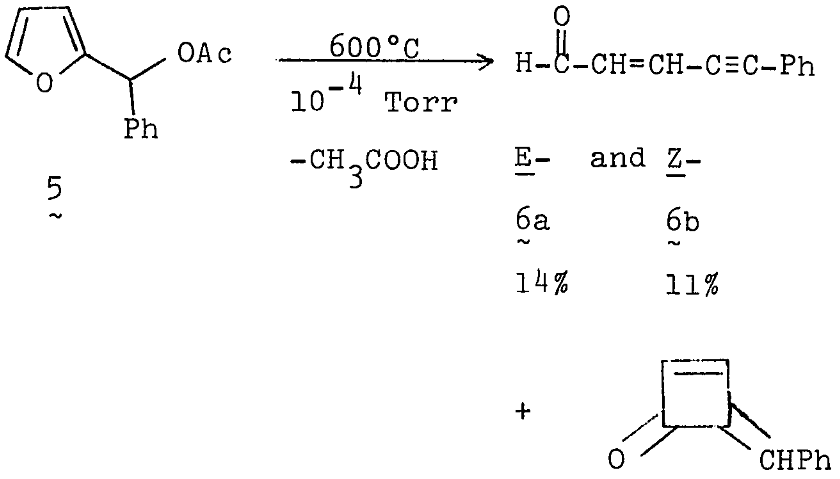
In order to determine the scope of the reaction and to achieve a better understanding of its mechanism, the pyrolysis of a series of substituted furfuryl esters was undertaken.[5-7] A mechanism for the conversion of 1a to 2a was proposed on the basis of a deuterium-labeling experiment, 1b to 2b and on a study of the pyrolysis products formed from 5-methylfurfuryl benzoate (3).[5]



3

4 (43%)

The favored mechanism explaining the formation of the pyrolysis products from 1 is thought to involve α eliminations of benzoic acid after zero to two [3,3] sigmatropic shifts of the benzoate group around the furan ring. Support for this mechanism was obtained by studying the pyrolysis products formed from α-phenylfurfuryl acetate (5).[6]

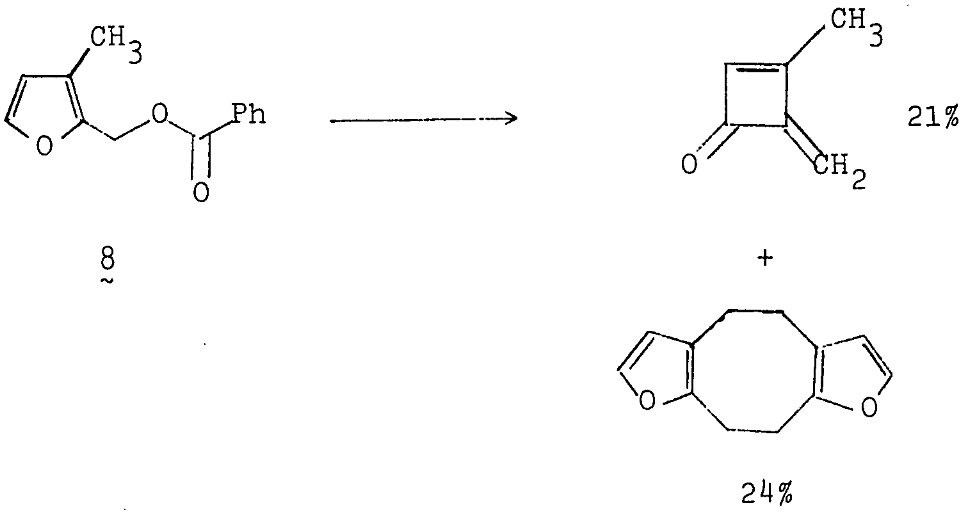


5

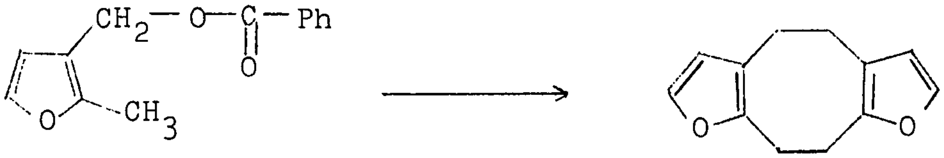
E- and Z-
6a 6b
14% 11%

E- and Z-
7a 7b
12% 9%

Experiments involving deuterium-labeling on the α carbon of 5 were performed in order to clarify the mechanisms for the formation of 6 and 7 from 5. Further support for the migration mechanism came from a study of the pyrolysis products formed from 3-methylfurfuryl benzoate (8) and 2-methyl-3-furylmethyl benzoate (9).[7]

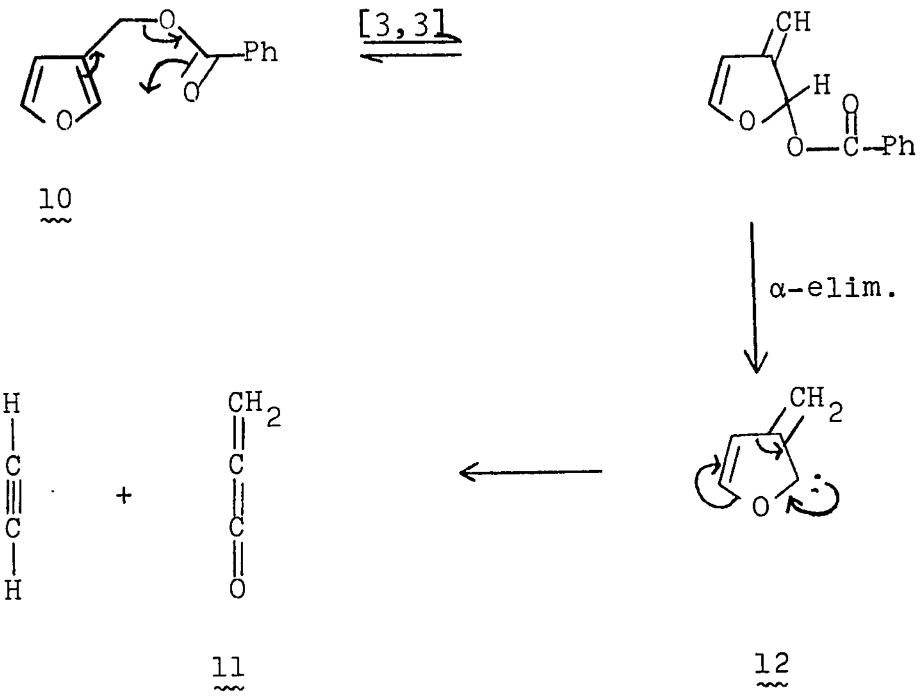


8



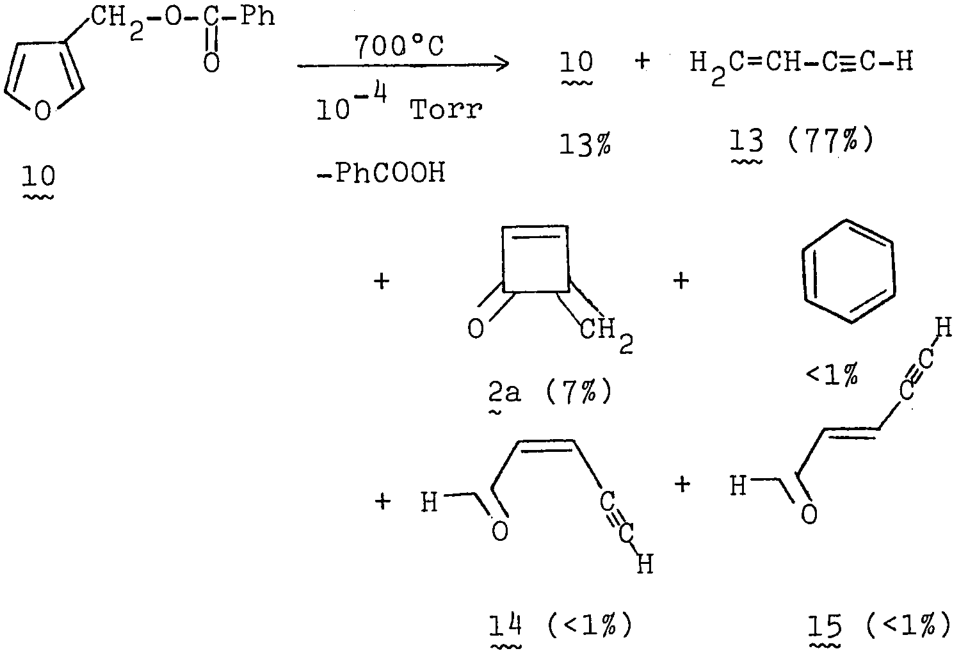
9

Consideration of the mechanism proposed for the formation of 2 from 1 suggested that the pyrolysis of 3-furylmethyl benzoate (10) might lead to the formation of acetylene and methyleneketene (11) after initial formation of carbene intermediate 12. Although methyleneketene (11) has been observed as a transient intermediate, the chemistry of 11 and its substituted derivatives has not been studied in detail.[8-10] This paper describes the results of a study of the pyrolysis chemistry of 10 at several temperatures.



RESULTS

3-Furylmethyl benzoate (10) was prepared by esterifying 3-furylmethyl alcohol with benzoyl chloride in the presence of triethylamine. Compound 10 was pyrolyzed using the method previously reported[7] at temperatures ranging from 600 to 750°C. The major products formed were vinylacetylene (13) and methylenecyclobutenone (2a). These products were accompanied by the formation of benzoic acid and trace amounts (<1% each) of benzene and *cis* and *trans*-2-penten-4-ynal (14 and 15). The product mixtures were readily separated by gas chromatography using a 25 meter, methylsilicone-coated, capillary column. There was no evidence at any pyrolysis temperature for the production of acetylene and methyleneketene (11).



The structure of 13 was indicated by its spectral properties. A gas chromatography/mass spectral analysis (GLC/MS) gave m/e peaks consistent with a molecular formula C_4H_4. The IR, ^1H NMR and ^{13}C NMR spectra were consistent with previously reported spectral data.[11-13]

The structure of 2a was also indicated by its spectral properties. GLC/MS analysis indicated a parent ion at m/e 80 corresponding to a molecular formula of C_5H_4O. The ^1H NMR chemical shifts were consistent with those previously reported for 2a.[1] The IR spectrum included a peak at 1787 cm^{-1} which is consistent with the carbonyl absorption previously reported for 2a (1783 cm^{-1}).[1] The ^{13}C NMR spectrum included peaks at δ 188.7 for the carbonyl carbon, δ 158.0 for the ring carbon attached to the exocyclic methylene group, δ 153.4 and 172.5 for the ring carbons which are α and β to the carbonyl group and δ 98.13 for the exocyclic methylene carbon.

The minor products were identified by GLC retention time and GLC/MS analyses. Products 14 and 15 were previously observed as minor products in the pyrolysis of furfuryl benzoate (1a).[5]

The product yields from the pyrolysis of **10** at temperatures ranging from 600 to 750°C (50°C intervals) were determined by ^{1}H NMR analysis, using benzyl ether as an internal standard, and are presented in Table I. As the pyrolysis temperature was increased from 600 to 750°C, the ratio of vinylacetylene (**13**) to methylenecyclobutenone (**2a**) increased from 5.8 to 15.6.

Table I. Products and yields formed from pyrolyses of 3-furylmethyl benzoate (10) at various temperatures

Pyrolysis Temp. (°C)	Products and Yields (%)[a]			Recovered Starting Material (%)[a]	Ratio[b]
	VA[c]	MCB[c]	BA[c]		
	13	2a			
600	11.5	<2	15	85	5.75
650[d]	41	6	40	53	6.83
700[d]	76.8	7.3	87	12.6	10.52
750[d]	82.8	5.3	90	--	15.56

[a] Yields were determined by ^1H NMR spectroscopy using benzyl ether as an internal standard.

[b] Ratio of the amount of vinylacetylene (13) to the amount of methylenecyclobutenone (2a) formed during the pyrolysis of 10.

[c] VA = vinylacetylene; MCB = methylenecyclobutenone; BA = benzoic acid.

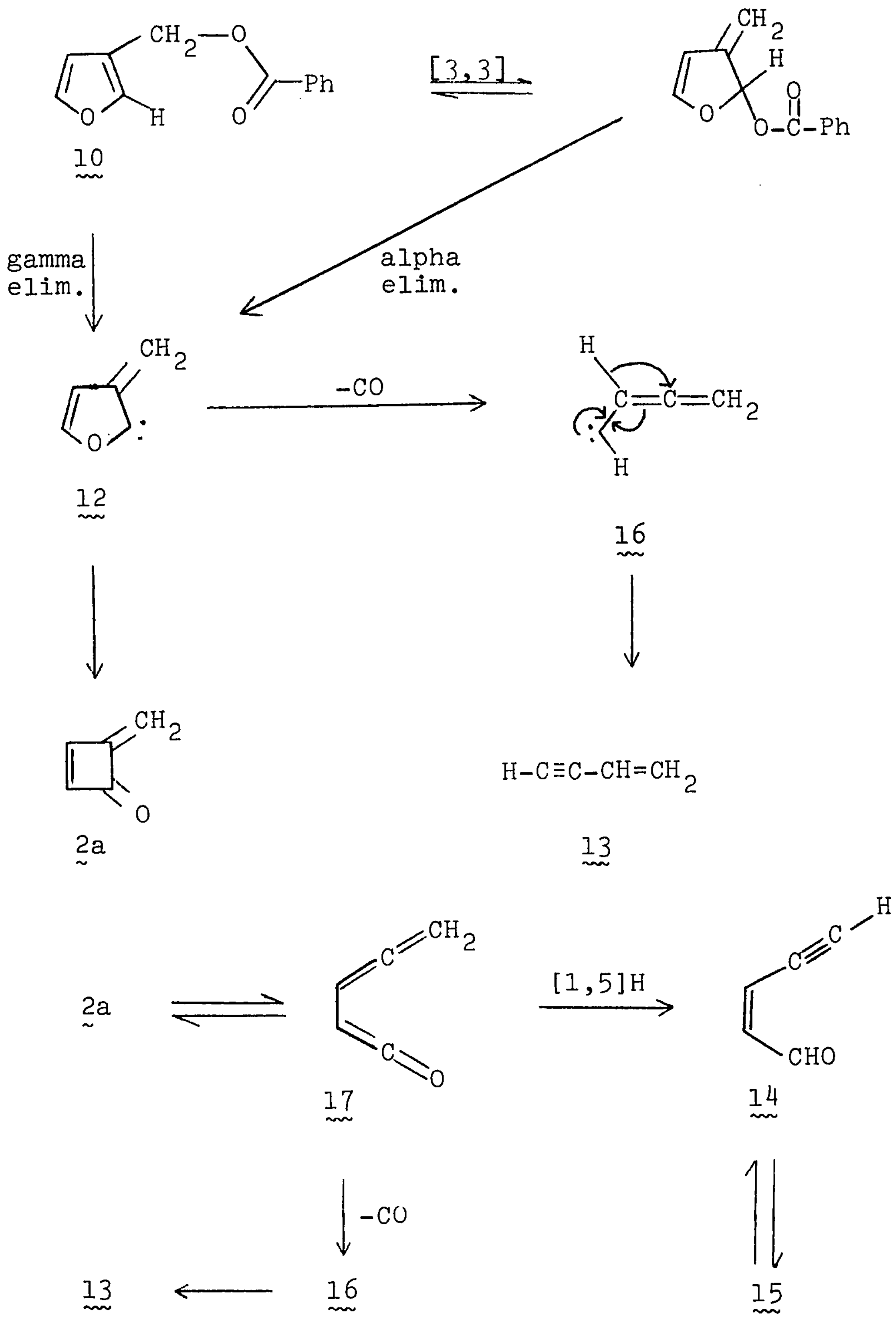
[d] In addition to the major products were minor amounts of benzene and *cis*- and *trans*-2-penten-4-ynal (<1% each).

DISCUSSION

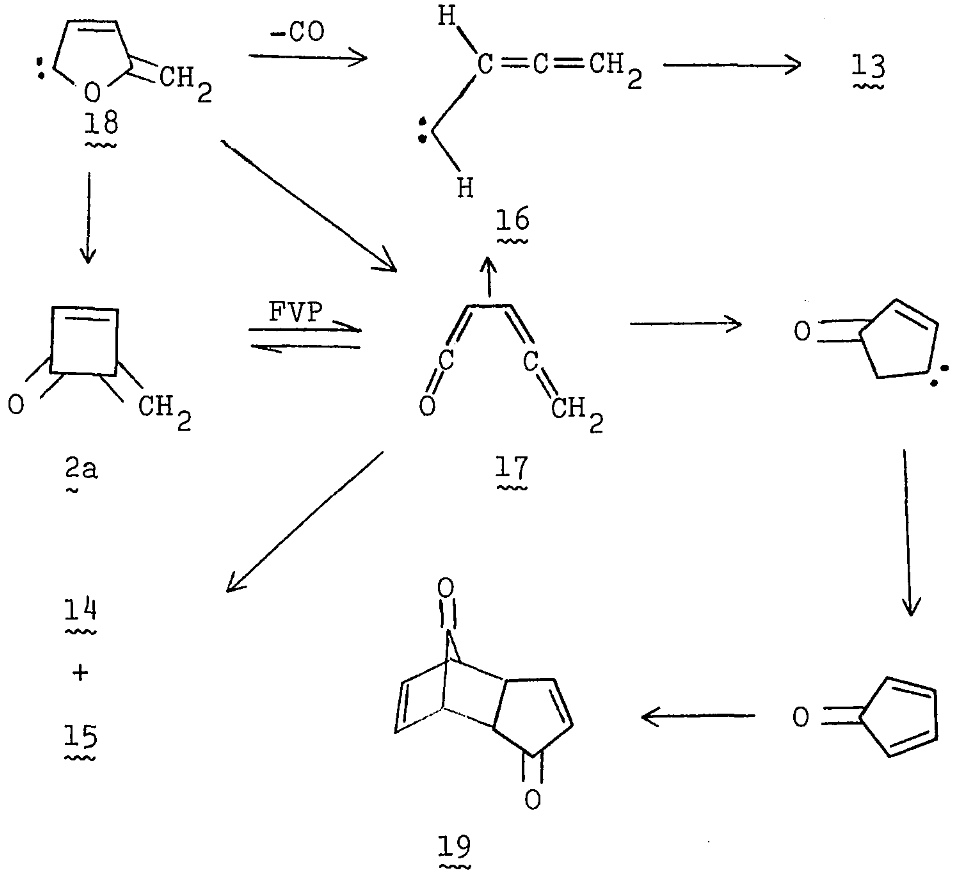
A migration mechanism was previously proposed for the conversion of furfuryl benzoate (1a) to methylenecyclobutenone (2a).[5] A mechanism which accounts for the formation of the pyrolysis products from 3-furylmethyl benzoate (10) is presented in Scheme I. The production of 2a can be explained by a multistep mechanism involving initially either a direct gamma elimination of benzoic acid from 10 forming carbene intermediate 12 or a two step mechanism involving a [3,3] sigmatropic shift of the benzoate group followed by alpha elimination of benzoic acid, producing 12. Since there is no literature precedent for this type of gamma elimination of a carboxylic acid, the two-step mechanism for the formation of 12 considered the more likely mechanism. Carbene intermediate 12 then undergoes a ring contraction to form 2a.

The production of vinylacetylene (13) can be explained by the explusion of a molecule of carbon monoxide from 12 producing allenyl carbene (16). Carbene 16 then undergoes rearrangement forming 13. Minor amounts of 13 may be formed by an alternative mechanism involving initially a conrotatory ring opening of 2a producing allenylketene (17), which loses a molecule of carbon monoxide forming 16. Carbene 16 then

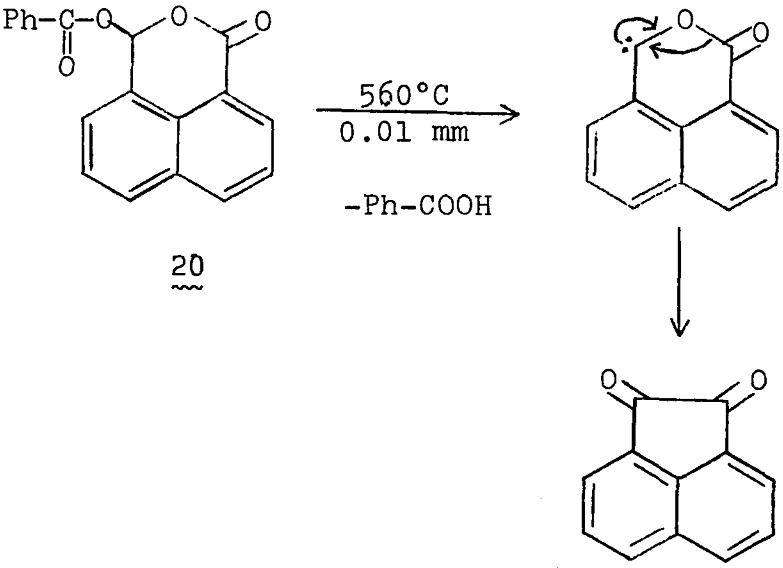
Scheme I


10
[3,3]
gamma elim.
alpha elim.
12
-CO
16
2a
H-C≡C-CH=CH2
13
2a
17
[1,5]H
14
-CO
13
16
15

undergoes rearrangement yielding 13. The loss of carbon monoxide from 12 is analogous to the loss of carbon monoxide from carbene intermediate 18, which is a possible source of the vinylacetylene (13) formed during the pyrolysis of furfuryl benzoate (1a) at temperatures above 650°C.[14] An alternative explanation for the formation of vinylacetylene (13) from furfuryl benzoate (1a) involves a conrotatory ring opening of the initially formed methylenecyclobutenone (2a), followed by loss of a molecule of carbon monoxide to form allenylcarbene (16). Intermediate 16, formed in both mechanisms, rearranges to vinylacetylene (13). The failure to detect the presence of the dimer 19 of cyclopentadienone among the pyrolysis products of 10 indicates that the mechanism involving conversion of 2a to 13 is at best a minor reaction pathway, since 19 is a product of the pyrolysis of methylenecyclobutenone (2a), along with compounds 13, 14, and 15.[15] This conclusion is supported by the observation that only trace amounts (<1% each) of 14 and 15 were formed during the pyrolyses of 10.



The isomerization of allylic esters via [3,3] sigmatropic shifts of a carboxylate group has been well documented[16-25] and in several systems, the initially formed [3,3] shift products have been isolated.[16,19-25] α-Elimination reactions have generally been observed in the pyrolysis of esters which can't undergo a β-elimination reaction.[1,5,6,26-30] The formation of methylenecyclobutenone (2a) from carbene intermediate 12 has literature precedent in the conversion of benzoyloxylactone 20 to dione 21.[30]



20

21 (71%)

EXPERIMENTAL

Methods and Materials. The pyrolysis apparatus has been previously described.[31] ^{1}H NMR spectra were recorded on Varian A-60, HA-100 or Hitachi-Perkin Elmer R-20B spectrometers. ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer. Chemical shifts are recorded in parts per million (δ) from tetramethylsilane (TMS). Infrared spectra were measured with a Beckman 4250 spectrophotometer. High resolution mass spectra were measured with an Associated Electronics Industries MS-902 instrument at 70 eV. Gas chromatography/mass spectral analyses (GLC/MS) were performed using a Finnigan 4000 instrument at 70 eV and an INCOS 2300 data system. GLC analyses were performed using a Hewlett Packard HP 5840A instrument equipped with a 25 meter, methylsilicone-coated, capillary column.

3-Furylmethyl alcohol was obtained from Aldrich Chemical Co. (listed as 3-furanmethanol). Benzoyl chloride and triethylamine were obtained from Eastman Organic Chemicals.

3-Furylmethyl Benzoate (**10**). A solution of 5.4703 g (0.0389 mole) of benzoyl chloride in 10 mL of dry ether ($LiAlH_4$) was added dropwise over a 15 minute period to a stirred solution of 3.5312 g (0.0360 mole) of 3-furylmethyl alcohol and 5.29 g (0.05 mole) of triethylamine in 80 mL of dry ether. After stirring the mixture for 11 h at room temperature, 10 mL of water was added and the mixture was stirred for an additional 4 h period. The layers were separated and the aqueous layer was extracted with ether (3 x 10 mL). The organic layers were combined and then washed successively with water (4 x 25 mL), 1 M hydrochloric acid (3 x 20 mL), saturated sodium bicarbonate (3 x 25 mL) and saturated sodium chloride (3 x 25 mL). After the organic layer was dried ($MgSO_4$), the solvent was removed giving the crude product (7.2805 g; 0.0360 mole; quantitative yield) which was purified by distillation, yielding 6.0293 g (0.030 mole; 83%) of 10: bp 73-74°C (0.03 mm), IR (thin film) 1720, 1600, 1584, 1500, 1450, 1275, 1105, 1020, 870, 790 cm^{-1}; ^{1}NMR ($CDCl_3$) δ 8.25-7.8 (m, 2H), 7.7-7.15 (m, 5H), 6.5 (m, 1H), 5.23 (s, 2H); high resolution mass spectrum calcd for $C_{12}H_{10}O_3$ 202.06300, measured 202.06280.

General Pyrolysis Procedure. Pyrolyses were run at furnace temperatures from 600 to 750°C. A sample of the furylmethyl ester in a Pyrex boat was placed into the sample compartment and the system was evacuated to ca. 10^{-4} Torr. The sample chamber was heated to ca. 85°C during the pyrolysis. A condenser cooled to ca. -20°C was inserted between the furnace and the liquid-nitrogen-cooled trap to collect the unreacted starting material and the benzoic acid formed as a byproduct. During the pyrolysis, 2 mL of a 1:1 mixture of carbon disulfide (CS_2) and deuterochloroform ($CDCl_3$) was deposited onto the trap through a side arm. After all of the starting material had distilled away from the sample compartment, nitrogen was introduced into the system and a known amount of benzyl ether was added as an internal standard. The trap was then warmed to -78°C and 2 mL of a 1:1 mixture of CS_2 and $CDCl_3$ was used to rinse the material on the walls of the trap to the bottom. The product solution was mixed with the standard by rinsing the walls of the trap ca. ten times with the solution using a cold pipette (CS_2 at -78°C). Most of the product solution was placed into four 5mm, NMR tubes at -78°C and NMR spectra were recorded after the samples were slowly warmed to room temperature. The remainder of the product solution was used for GLC analysis.

The condenser was washed with ca. 50 mL of ether. After removal of the solvent and addition of a known amount of benzyl ether as a standard, NMR spectra were recorded for the condenser contents.

Pyrolysis of 3-Furylmethyl Benzoate (10). Pyrolyses were carried out with ca. 0.4 g of 10 at 600, 650, 700 and 750°C using the general procedure. Yields of recovered starting material 10, as well as products 2a and 13 were determined by quantitative ^{1}H NMR analysis using benzyl ether as an internal standard. Yields of the minor products (benzene, 14 and 15) were determined by GLC analysis using a 25 m, methylsilicone-coated capillary column (column temperature 40°C for 15 min followed by temperature programming at a rate of 5°C per minute until a temperature of 175°C was reached). Yields of the pyrolysis products from 10 are presented in Table I. The products were identified from the following data.

Vinylacetylene (13): IR (CS_2) 3305, 2280, 725, 700 cm^{-1}, [lit.[11] IR (ether) 3300, 2110, 1600 cm^{-1}]; ^{1}H NMR (CS_2) δ 5.8-5.34 (m, 3H), 2.76 (m, 1H), [lit.[12] ^{1}H NMR (CCl_4) δ 5.85-5.35 (m, 3H), 2.88 (broad s, 1H)]; ^{13}C NMR (1:1 $CS_2/CDCl_3$) δ 127.58, 116.4, 82.25, 78.01, [lit.[13] ^{13}C NMR (acetone-d_6) δ 129.2, 117.3, 82.8, 80.0]; GLC/MS m/e (relative intensity) 54.10 (0.10), 53.10 (4.04), 52.08 (100.00), 51.10 (16.27), 50.06 (7.05).

Methylenecyclobutenone (2a): IR (CS_2) 1787, 1690, 815 cm^{-1}, [lit.[1] IR ($CDCl_3$) 1783, 1688, 823 cm^{-1}]; ^1H NMR (CS_2) δ 8.59 (d, J = 2 Hz, 1H), 7.02 (d, J = 2 Hz, 1H), 5.04 (m, 1H), 4.76 (m, 1H), [lit.[1] ^1H NMR (ethyl acetate) δ 8.66 (m, 1H), 7.16 (m, 1H), 5.01 (m, 1H), 4.78 (m, 1H)]; GLC/MS m/e relative intensity) 81.0 (3.22), 80.0 (38.97), 75.9 (5.37), 54.0 (4.13), 53.0 (4.84), 52.1 (100.00), 51.0 (16.13), 50.0 (7.26).

Benzene: ^1H NMR (CS_2) δ 7.25 (s, 6H); GLC/MS m/e (relative intensity) 79.0 (6.15), 78.0 (100.00), 66.0 (0.49), 52.0 (2.19), 39.0 (1.26); GLC retention time matched that observed for an authentic sample of benzene.

cis-2-Penten-4-ynal (14): GLC/MS m/e (relative intensity) 80.0 (0.44), 79.0 (1.64), 53.0 (3.29), 52.0 (100.00), 51.0 (13.19), 50.0 (2.91); GLC retention time matched that of a sample of 14 prepared by the FVP of furfuryl benzoate (1a).[1,5]

trans-2-Penten-4-ynal (15): GLC/MS m/e (relative intensity) 81.0 (1.54), 80.0 (49.45), 79.0 (11.54), 53.0 (2.64), 52.0 (100.00), 51.0 (23.96), 50.0 (5.44); GLC retention time matched that of a sample of 15 prepared by the FVP of furfuryl benzoate (1a).[1,5]

REFERENCES

1. Trahanovsky, W. S.; Park, M.-G *J. Am. Chem. Soc.* 1973, 95, 5412.
2. DeSelms, R. C.; Delay, F. *J. Am. Chem. Soc.* 1973, 95, 274.
3. Cava, M. P. "Cyclobutadiene and Related Compounds"; Academic Press: New York, 1967; p 157-158.
4. For alternate routes to cyclobutane derivatives see:
    a) Brady, W. T.; Stockton, J. D.; Patel, A. D. *J. Org. Chem.* 1974, 39, 236.
    b) Bampfield, H. A.; Brook, P. R.; Hunt, K. *Chem. Commun.* 1976, 146.
    c) Spangler, R. J.; Kim, J. H.; Cava, M. P. *J. Org. Chem.* 1977, 42, 1697.
    d) Snider, B. B; Brown, L. A.; Eichen Conn, R. S.; Killinger, T. A. *Tetrahedron Lett.* 1977, 2831.
    e) Trost, B. M.; Scudder, P. H. *J. Am. Chem. Soc.* 1977, 99, 7601.
5. Trahanovsky, W. S.; Park, M.-G. *J. Org. Chem.* 1974, 39, 1448.
6. Trahanovsky, W. S.; Alexander, D. L. *J. Am. Chem. Soc.* 1979, 101, 142.
7. Trahanovsky, W. S.; Cassady, T. J.; Woods, T. L. *J. Am. Chem. Soc.* 1981, 103, 6691.
8. Brown, R. F. C.; Eastwood, F. W.; McMullen, G. L. *J. Am. Chem. Soc.* 1976, 98, 7421.
9. Brown, R. F. C.; Eastwood, F. W.; McMullen, G. L. *Aust. J. Chem.* 1977, 30, 179.
10. Blackman, G. L.; Brown, R. D.; Brown, R. F. C.; Eastwood, F. W.; McMullen, G. L.; Robertson, M. L. *Aust. J. Chem.* 1978, 31, 209.

11. Montijn, P. P.; Brandsma, L.; Arens, J. F. Recl. Trav. Chim. Pays-Bas 1967, 86, 129.

12. Trahanovsky, W. S.; Emeis, S. L. J. Am. Chem. Soc. 1975, 97, 3773.

13. Kowalewski, J.; Granberg, M.; Karlsson, F.; Vestin, R.; J. Magn. Res. 1976, 21, 331.

14. Trahanovsky, W. S.; Cassady, T. J.; Amah, A. Unpublished results, Department of Chemistry, Iowa State University, Ames, Iowa.

15. Trahanovsky, W. S.; Amah, A. Unpublished results, Department of Chemistry, Iowa State University, Ames, Iowa.

16. Bailey, W. J.; Barclay, R., Jr. J. Org. Chem. 1956, 21, 328.

17. a) Grummitt, O.; Splitter, J. J. Am. Chem. Soc. 1952, 74, 3924.

    b) Grummitt, O.; Mandel, Z. J. Am. Chem. Soc. 1956, 78, 1054.

18. Bailey, W. J.; Goossens, J. C. J. Am. Chem. Soc. 1956, 78, 2804.

19. a) Greenwood, F. L. J. Org. Chem. 1959, 24, 1735.

    b) Greenwood, F. L. J. Org. Chem. 1962, 27, 2308.

20. Marvel, C. S.; Brace, N. O. J. Am. Chem. Soc. 1948, 70, 1775.

21. Landor, P. D.; Landor, S. R. J. Chem. Soc. 1956, 1015.

22. Heilbron, I. M.; Jones, E. R. H.; McCombie, J. T.; Weedon, B. C. J. Chem. Soc. 1945, 88.

23. Burton, H. J. Chem. Soc. 1928, 1650.

24. Balfe, M. P.; Kenyon, J. Trans. Faraday Soc. 1941, 37, 721.

25. a) Braude, E. A.; Turner, D. W.; Waight, E. S. J. Chem. Soc. 1958, 2396.

    b) Braude, E. A.; Turner, D. W. J. Chem. Soc. 1958, 2404.

26. a) Kwart, H.; Hoster, D. P. Chem. Commun. 1967, 1155.

    b) Kwart, H.; Ling, H. G. Chem. Commun. 1969, 302.

27. Lehr, R. E.; Wilson, J. M. Chem. Commun. 1971, 666.

28. Hoffmann, R. W.; Schuttler, R.; Loff, I. H. Chem. Ber. 1977, 110, 3410.

29. Oele, P. C.; Louw, R. Tetrahedron Lett. 1972, 4941.

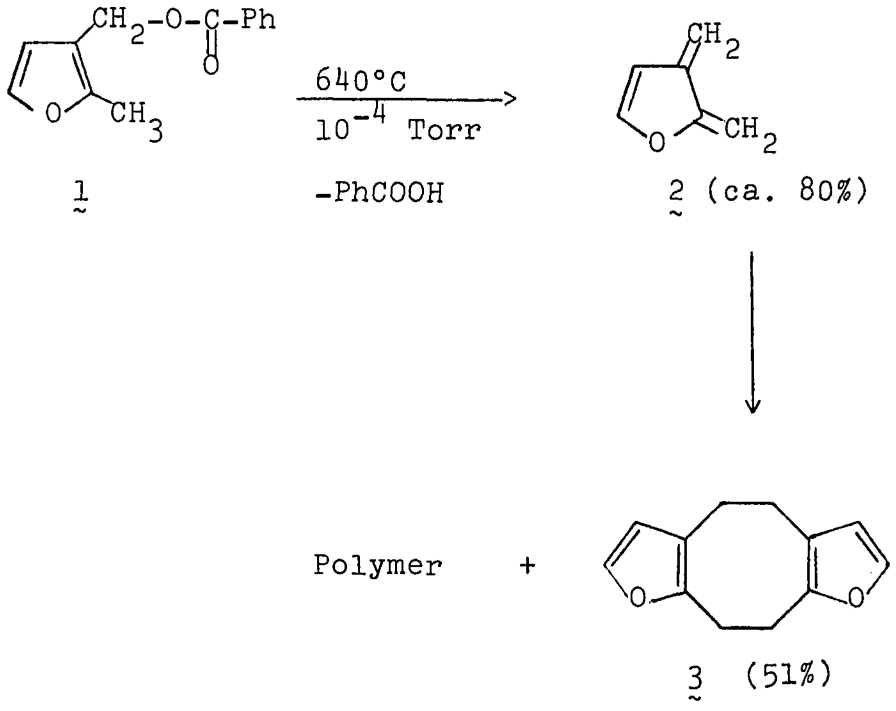
30. Brown, R. F. C.; Eastwood, F. W.; Lim, S. T.; McMullen, G. L. Aust. J. Chem. 1976, 29, 1705.

31. Trahanovsky, W. S.; Ong, C. C.; Pataky, J. G.; Weitl, F. L.; Mullen, P. W; Clardy, J. C.; Hansen, R. S. J. Org. Chem. 1971, 36, 3575.

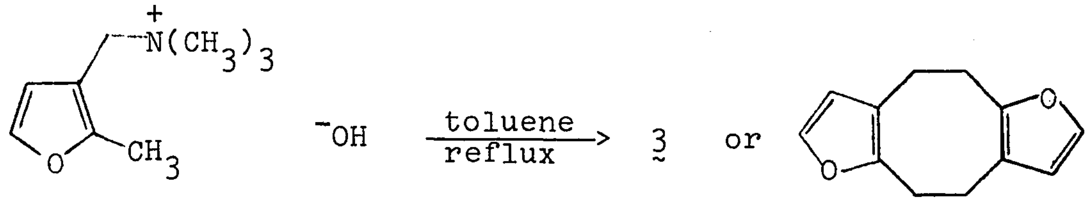
SECTION V. CHEMISTRY OF FURANORADIALENE PREPARED BY THE FLASH VACUUM PYROLYSIS OF DIESTERS OF 3,4-BIS(HYDROXYMETHYL)-2,5-DIMETHYLFURAN

INTRODUCTION

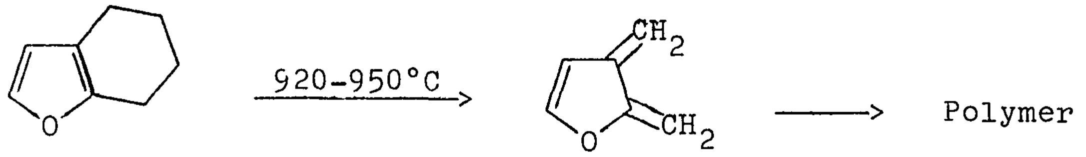
Recently we reported that the flash vacuum pyrolysis (FVP) of 2-methyl-3-furylmethyl benzoate (**1**) gives good yields of 2,3-dimethylene-2,3-dihydrofuran (**2**).[1] Compound **2** is an air-sensitive material which readily undergoes dimerization, forming the head-to-head, [4+4] dimer (**3**).



Although **2** has been previously postulated as an intermediate in the liquid-phase pyrolysis of (2-methyl-3-furylmethyl)-trimethylammonium hydroxide (**4**)[2] and the gas-phase pyrolysis of tetrahydrobenzofuran (5),[3] the FVP of methyl-substituted, furylmethyl esters is the best method currently available for generating solutions of dimethylenedihydrofurans.[1]



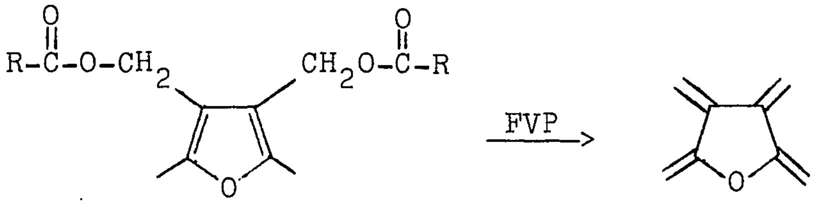
4



5

2

In order to test the generality of this method, a study of the pyrolysis reactions of diester derivatives 6 of 3,4-bis(hydroxymethyl)-2,5-dimethylfuran (7) was undertaken. If the mechanism proposed for the conversion of 1 to 2[1] is valid, the pyrolysis of 6 should produce furanoradialene (8) by the independent loss of two molecules of the corresponding carboxylic acid.



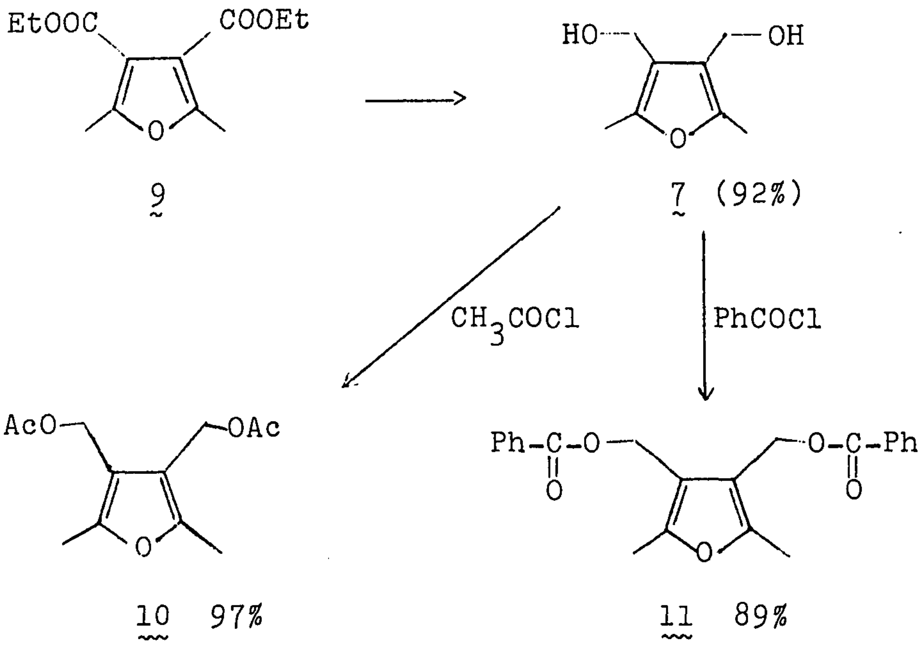
6

8

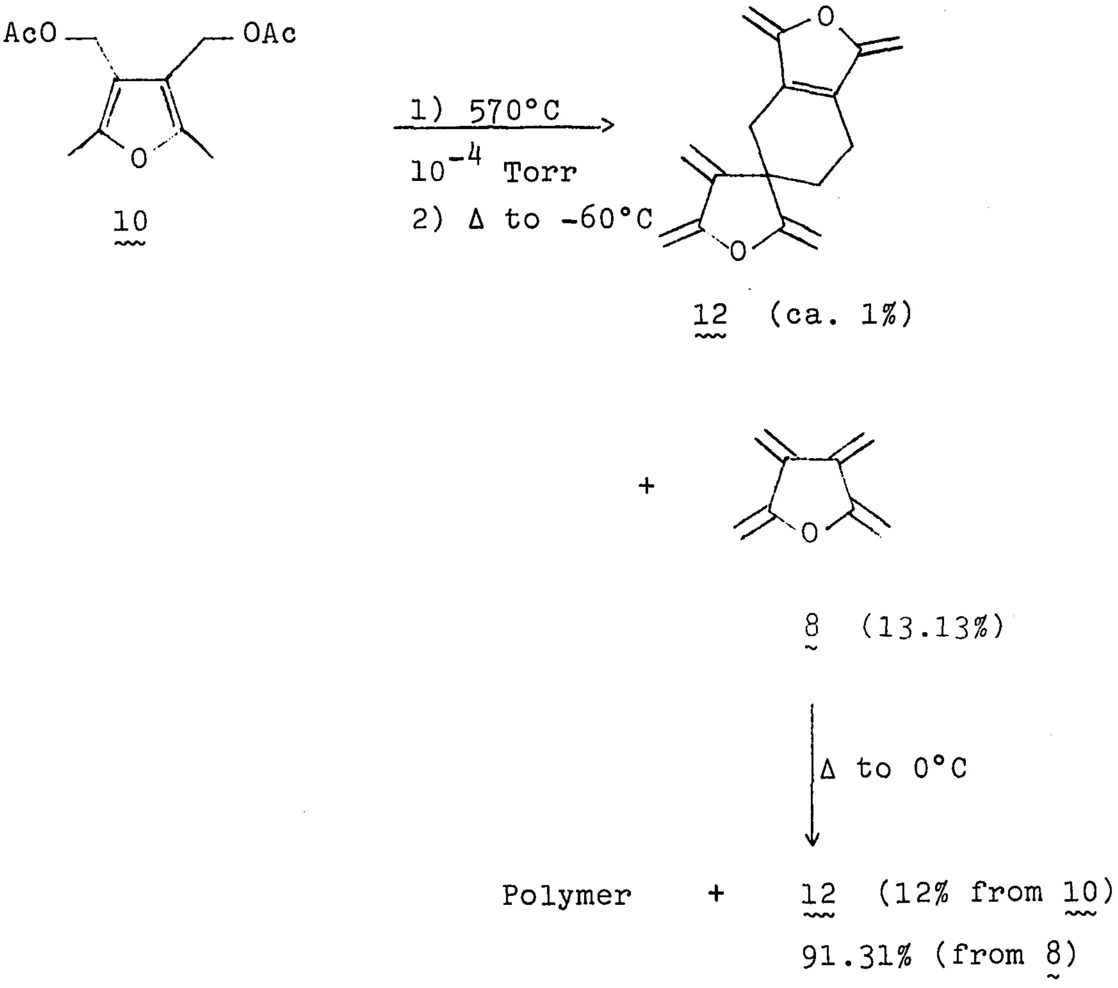
Furanoradialene (8) is the furan analog of the radialenes, a class of compounds characterized by having a carbocyclic ring in which each carbon is part of an exocyclic, carbon-carbon double bond.[4] The parent radialenes which have been synthesized and studied to date are [3] radialene,[5-18] [4] radialene,[19-24] [6] radialene,[25-27] naptharadialene,[4] and furanoradialene (8).[28] Although the parent radialenes are air sensitive materials which are highly reactive, several stable substituted radialenes have been reported.[29-40]

RESULTS

3,4-Bis(hydroxymethyl)-2,5-dimethylfuran (**7**) was prepared in 92% yield by reducing diethyl 2,5-dimethyl-3,4-furandicarboxylate (**9**)[41,42] with lithium aluminum hydride. Diol **7** was converted to diacetate **10** by treatment with acetyl chloride in the presence of triethylamine. Diol **7** was converted to dibenzoate **11** by similar treatment with benzoyl chloride.



Diacetate 10 was pyrolyzed at temperatures ranging from 450 to 650°C. None of the starting ester 10 was recovered between 570 and 650°C. Incomplete conversion of the starting material 10 was observed between 500 and 550°C and at temperatures below 500°C, only 10 was recovered. The FVP of 10 at each temperature produced a white product band in the liquid-nitrogen-cooled trap. During the pyrolyses, a 1:1 mixture of carbon disulfide (CS_2) and chloroform-d_1 ($CDCl_3$) was deposited into the trap through a side arm. After the trap contents were liquified by warming the trap to -78°C, ^1H and ^{13}C NMR spectra were recorded at -60°C. The samples were then warmed to 0°C and NMR spectral data were again recorded. In each experiment, the product mixtures kept below -60°C consisted mainly of furanoradialene (8) and polymer, along with trace amounts of one [4+2] dimer of 8, 12. When the samples were warmed to 0°C, the product mixtures consisted of polymer and [4+2] dimer 12. Although there are six possible [4+2] dimers of 8 (four resulting from the 2,3-dimethylene portion of 8 acting as the diene and two resulting from the 3,4-dimethylene portion of 8 acting as the diene), and four possible [4+4] dimers, no evidence for any other dimer of 8 was obtained. This conclusion is supported by the observation that 91% of the furanoradialene (8) present in the ^1H NMR samples is converted to [4+2] dimer **12** upon warming the samples to 0°C. The low yields of furanoradialene (**8**) obtained from the pyrolyses of **10** were due to the extensive polymerization which occurred in each experiment.



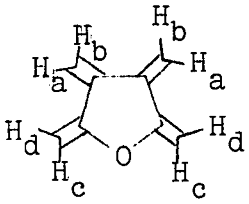
10

12 (ca. 1%)

8 (13.13%)

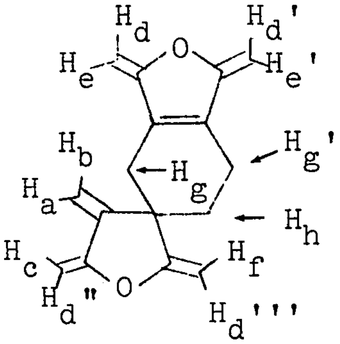
12 (12% from **10**)
91.31% (from **8**)

The structure of 8 was indicated by its spectral properties. The ^{1}H NMR spectrum included two-proton singlets at δ 5.55 and 5.52 for the exocyclic, methylene hydrogens at the three and four positions and two-proton doublets at δ 4.59 and 4.52 (J = 3 Hz) for the exocyclic, methylene hydrogens at the two and five positions. These chemical shifts are consistent with those previously reported for furanoradialene (8)[28] and are presented in Figure 1. The ^{13}C NMR spectrum of 8 included signals at δ 156.1 for ring carbons two and five, δ 135.8 for ring carbons three and four, δ 106.0 for the exocyclic, methylene carbons at ring positions three and four, and δ 81.9 for the exocyclic methylene carbons at ring positions two and five. The ^{13}C NMR chemical shifts observed for the ring carbons of 8 are consistent with those observed for ring carbons two and three in 2,3-dimethylene-2,3-dihydrofuran (2) [(1:1 $CS_2/CDCl_3$, -60° C) δ 157.62 and 139.63].[1] The ^{13}C NMR chemical shifts differ slightly from those previously reported for 8 which were taken from a ^{13}C NMR spectrum of a complex mixture containing 8 as a minor component.[28] The chemical shifts were incorrectly assigned by the authors to signals at δ 160.5 for ring carbons two and five and δ 156.6 for ring carbons three and four.



8

H_a = 5.55 (s, 2H)
H_b = 5.52 (s, 2H)
H_c = 4.59 (d, J = 3 Hz, 2H)
H_d = 4.52 (d, J = 3 Hz, 2H)



12

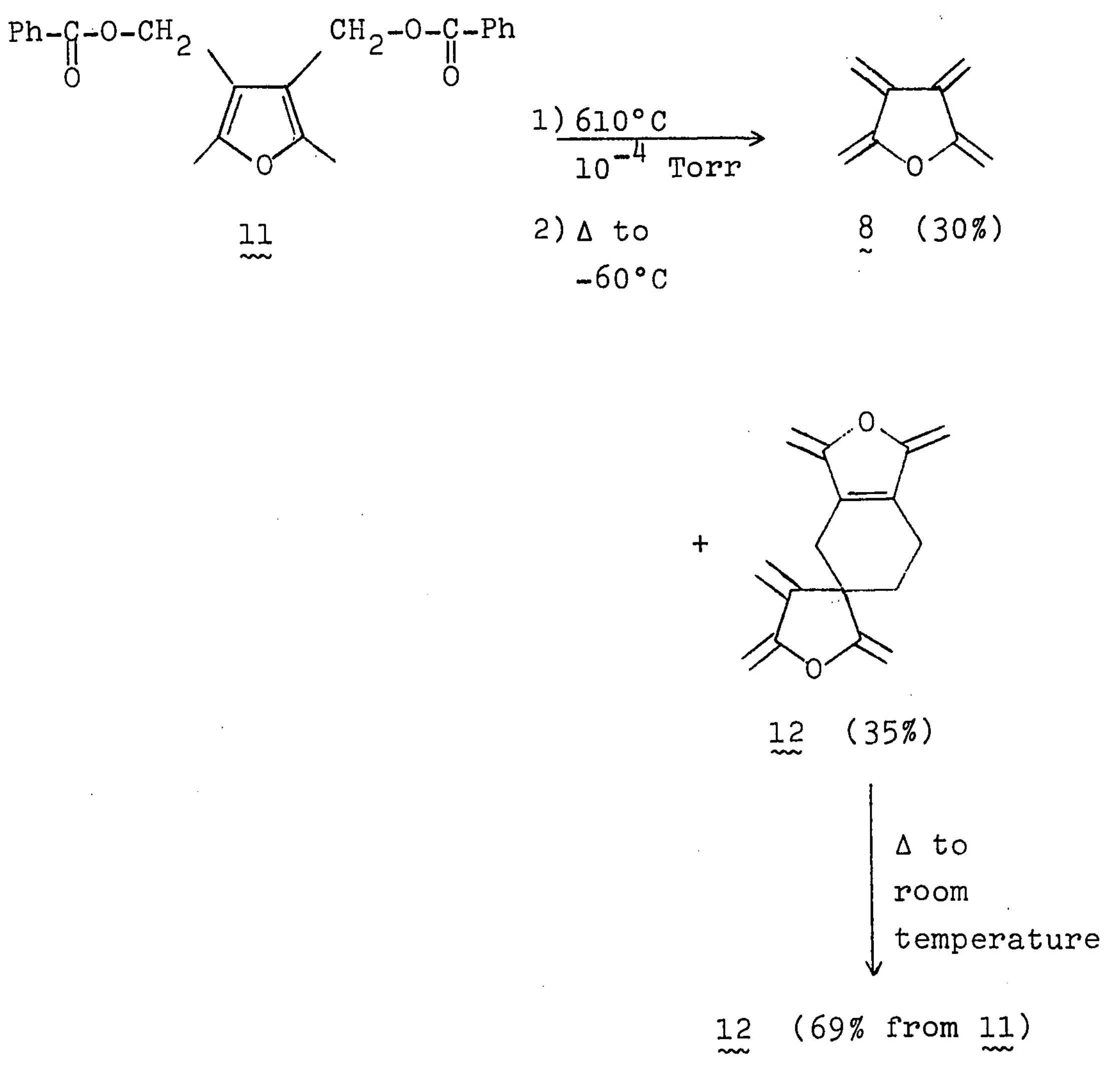
H_a = 5.5 (s, 1H)
H_b = 4.92 (s, 1H)
H_c = 4.54 (d, J = 2.5 Hz, 1H)
$H_d = H_{d'} = H_{d''} = H_{d'''}$
= 4.46 (d, J = 2.5 Hz, 4H)
$H_e = H_{e'}$ = 4.09 (m, 2H)
H_f = 3.94 (d, J = 2.5 Hz, 1H)
$H_g = H_{g'}$ = 2.55 - 2.27 (m, 4H)
H_h = 1.88 - 1.65 (m, 2H)

Figure 1. ^1H NMR chemical shifts of furanoradialene (8) recorded at -60°C (top) and the [4+2] dimer (12) of furanoradialene (8) recorded at room temperature (bottom) in 1:1 $CS_2/CDCl_3$ (δ from Me_4Si)

The structure of [4+2] dimer 12 was also indicated by its spectral properties. The ^1H NMR chemical shifts of 12 recorded at room temperature are presented in Figure 1. The ^{13}C NMR spectrum of 12 consisted of 16 peaks, with appropriate chemical shifts, including signals at δ 82.62, 81.48, 81.05 and 80.83 for the four exocyclic, methylene carbons at the two and five positions of the dihydrofuran and tetrahydrofuran rings. The ^{13}C NMR spectrum also included a peak at δ 106.72 for an exocyclic, methylene carbon at either the three or the four position of a tetrahydrofuran ring. The only dimer of 8 with structural features consistent with the observed ^1H and ^{13}C NMR chemical shifts is [4+2] dimer 12.

In order to improve the yield of furanoradialene (8), a study of the pyrolysis chemistry of 3,4-bis(benzoyloxymethyl)-2,5-dimethylfuran (11) was undertaken. The amount of polymer formed during the pyrolysis of 11 was expected to be less than the amount formed from 10 because of greater control of the rate of material transfer into the hot zone with dibenzoate 11 due to its higher boiling point than that of diacetate 10. Also, the benzoic acid formed as a biproduct from the pyrolysis of 11 is deposited onto a condenser at ca. -20°C inserted between the furnace and the liquid-nitrogen-cooled trap. The acetic acid formed from **10** is deposited into the liquid-nitrogen-cooled trap along with furanoradialene (**8**) and may cause some of the observed polymerization.

The pyrolysis of **11** at 610-620°C and ca. 10^{-4} Torr was carried out using the procedure described for the pyrolysis of **10**. The product mixtures kept below -60°C consisted of furanoradialene (**8**) and [4+2] dimer **12**, along with benzoic acid and a substantial amount of white polymeric material. After warming the product solution to room temperature, a 69% yield of [4+2] dimer **12** was formed from starting dibenzoate **11**. The ^{1}H and ^{13}C NMR chemical shifts for **8** and **12**, formed from **11**, matched those of samples of **8** and **12** formed from **10**. The ^{1}H NMR spectra of the pyrolysis products of **11**, recorded at -78 and -30°C, are presented in Figure 2.



11

8 (30%)

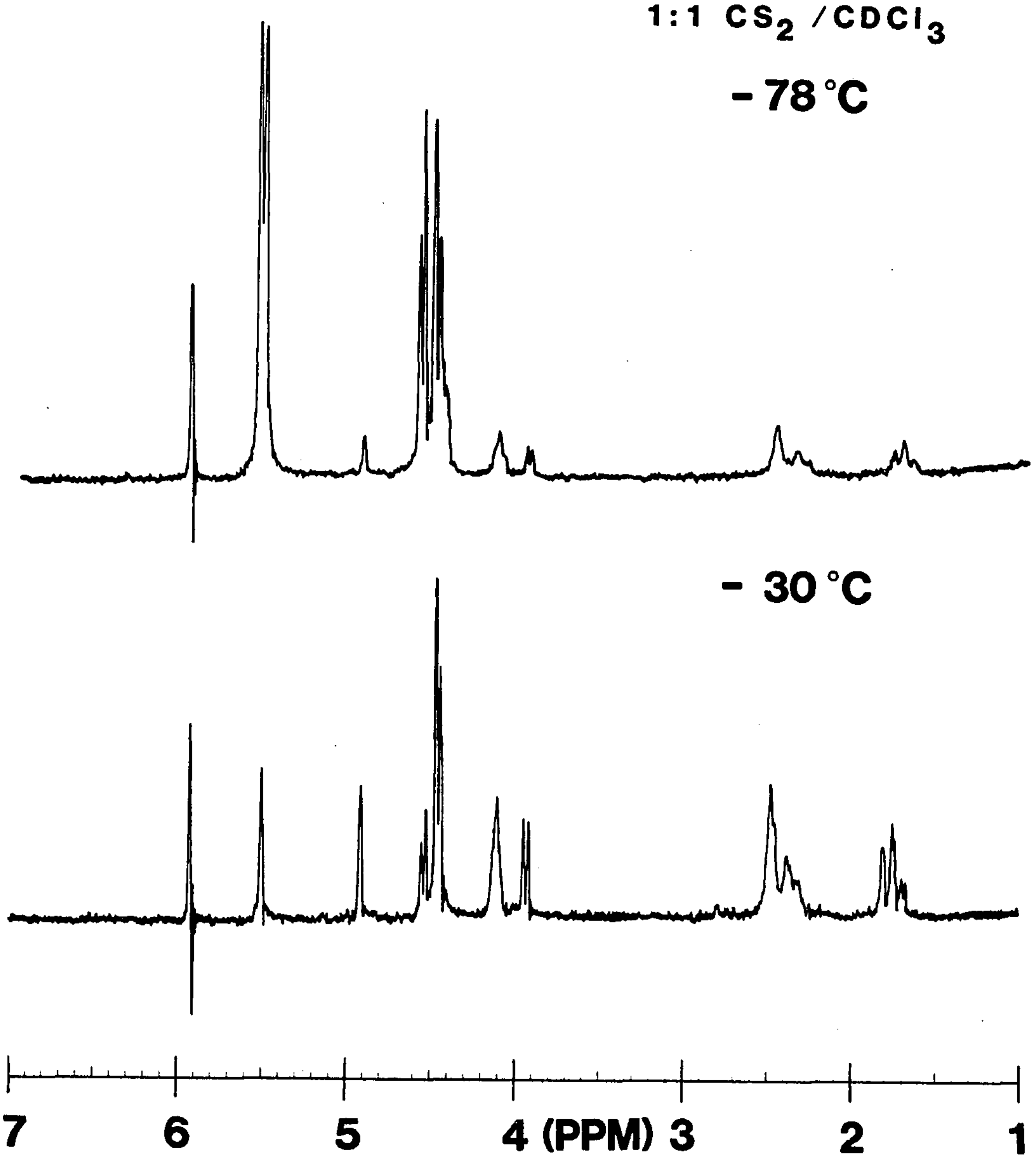
12 (35%)

12 (69% from 11)

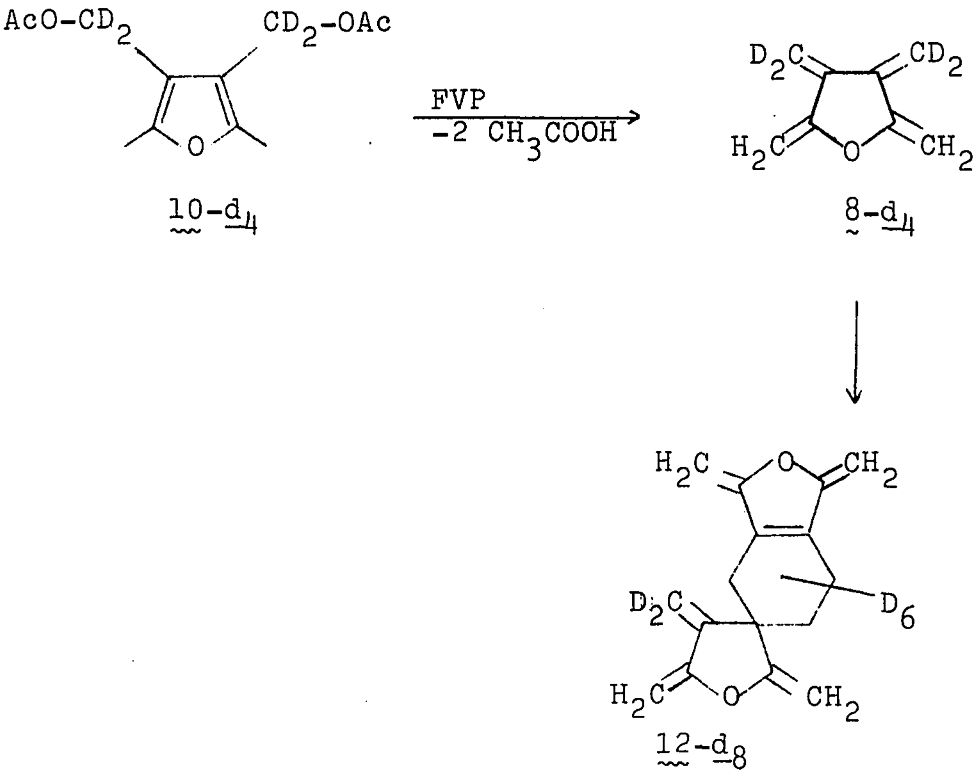
Figure 2. ^{1}H NMR spectra of the pyrolysis products formed from 3,4-bis(benzoyloxymethyl)-2,5-dimethylfuran (11) in 1:1 CS$_2$/CDCl$_3$ and in the presence of a 1,1,2,2-tetrachloroethane internal standard

Top: Spectrum of a mixture of furano-radialene (8) and [4+2] dimer 12 recorded at -78°C (mole ratio of 8 to 12 = 3.52)

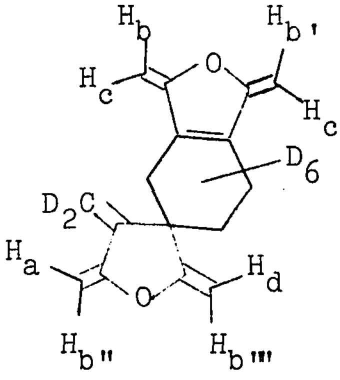
Bottom: Spectrum of [4+2] dimer 12 recorded at -30°C


1:1 CS_2 /$CDCl_3$
- 78 °C
- 30 °C
7
6
5
4 (PPM) 3
2
1

The preparation and pyrolysis of **10**-d_4 was undertaken in order to assign the ^1H and ^{13}C NMR chemical shifts for **8** and **12**. A mass spectral analysis of **10**-d_4 indicated greater than 96% d_4 incorporation. The ^1H and ^{13}C NMR spectra of



8-d_4 and **12**-d_8 were recorded at -60°C and at room temperature, respectively. The ^1H NMR spectrum of **8**-d_4 consisted of two-proton doublets ($J = 2.5$ Hz) at δ 4.61 and 4.52 for the exocyclic methylene hydrogens at the two and five positions. The ^{13}C NMR spectrum of **8**-d_4 included signals at δ 156.08 for ring carbons two and five, at δ 135.8 for ring carbons three and four and at δ 81.8 for the methylene carbons attached to ring positions two and five. Upon warming the sample to room temperature, **8**-d_4 dimerized, forming **12**-d_8. The ^1H NMR chemical shifts (1:1 $CS_2/CDCl_3$; δ from Me_4Si) of **12**-d_8 are presented below.

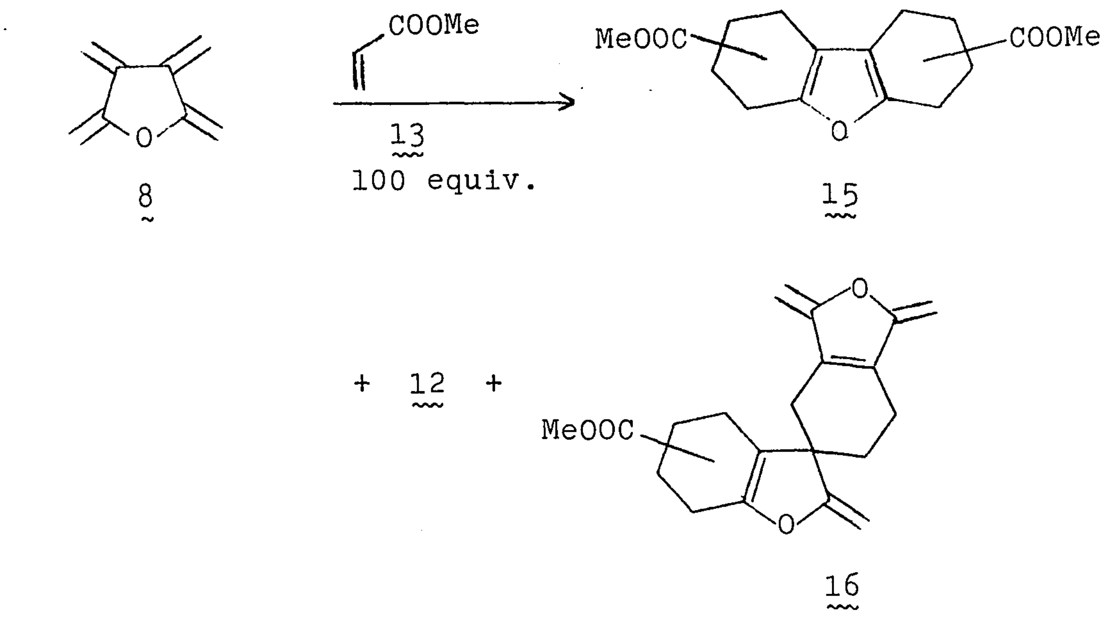


12-d_8

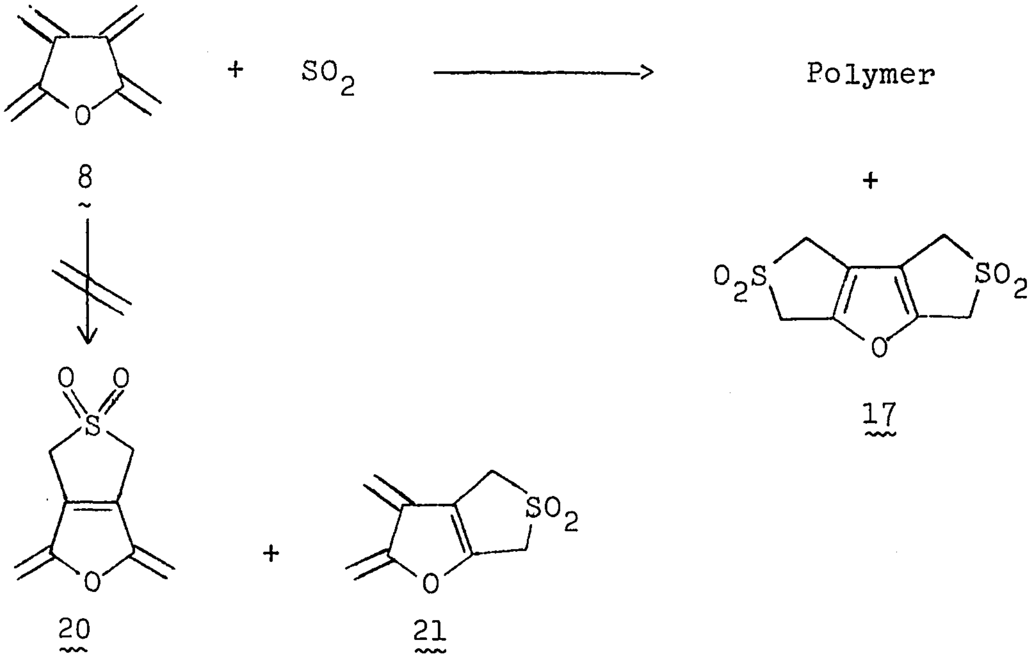
H_a = 4.53 (d, J = 2.5 Hz, 1H)
H_b = $H_{b'}$ = $H_{b''}$ = $H_{b'''}$
= 4.45 (d, J = 2.5 Hz., 4H)
H_c = $H_{c'}$ = 4.09 (m, 2H)
H_d = 3.92 (d, J = 2.5 Hz, 1H)

Most of the attempts to trap furanoradialene (**8**) with dienophiles such as methyl acrylate (**13**) and dimethyl acetylenedicarboxylate (**14**) resulted in the formation of [4+2] dimer **12**. A sample of furanoradialene (**8**), kept for 60 hours at temperatures below -70°C in the presence of ten equivalents of **14** formed only [4+2] dimer **12**. The relative amounts of furanoradialene (**8**), [4+2] dimer **12** and dienophile **14** were determined by low-temperature, ^1H NMR analyses at various times during the experiments. After warming the samples to room temperature, GLC and thin layer chromatographic analyses of the product mixtures gave no indication of the presence of a Diels-Alder adduct of 8 with 14. Similar results were obtained using ca. ten equivalents of methyl acrylate (13) as the dienophile.

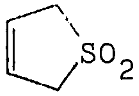
When dilute solutions of 8 were mixed with ca. 100 equivalents of methyl acrylate and maintained at temperatures below -72°C for 12 h, a diadduct (15) of 8 with methyl acrylate was formed along with [4+2] dimer 12 and trace amounts of a Diels-Alder adduct (16) of 12 with methyl acrylate. ^{1}H NMR analysis of the product mixture after workup indicated that 15 was the major product formed, along with smaller amounts of 12 and 16. Attempts to isolate 15 from the product mixtures by liquid chromatography (both TLC and column) on silica gel were unsuccessful due to decomposition of 12 and 16 under the separation conditions. Elution of the decomposition products occurred at rates comparable to the rate of elution of 15. There was no evidence in the ^{1}H NMR spectra for the formation of a mono adduct of furanoradialene (8) with methyl acrylate (13).

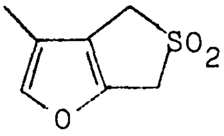


Several attempts to allow methylene chloride solutions of furanoradialene (8) to react at ca. -78°C with excess amounts of sulfur dioxide (SO_2) resulted in the formation of small amounts (less than 10%) of a diadduct 17 of furanoradialene (8) with SO_2, along with large amounts of a yellow-to-off-white colored, air-sensitive polymer. The structure of diadduct 17 was determined from its spectral properties. The IR spectrum included intense peaks at 1330 and 1110 cm^{-1} which are consistent with the SO_2 absorptions reported for 2,5-dihydrothiophene-1,1-dioxide (18) (1310 and 1130 cm^{-1})[43] and sulfone 19 (1322 and 1111 cm^{-1}).[44] The ^{1}H NMR spectrum included four-proton multiplets at δ 4.42 and 4.32 which



are consistent with the methylene signals observed for sulfone 19 (δ 4.22 and 4.14).[44] There was no ^{1}H NMR evidence for the formation of either the [4+2] dimer 12 of furanoradialene (8) or a monoadduct (20 or 21) of 8 with SO_2. Attempts to isolate the diadduct 17 by liquid chromatography (TLC and column) resulted in complete decomposition of the product mixtures.


18

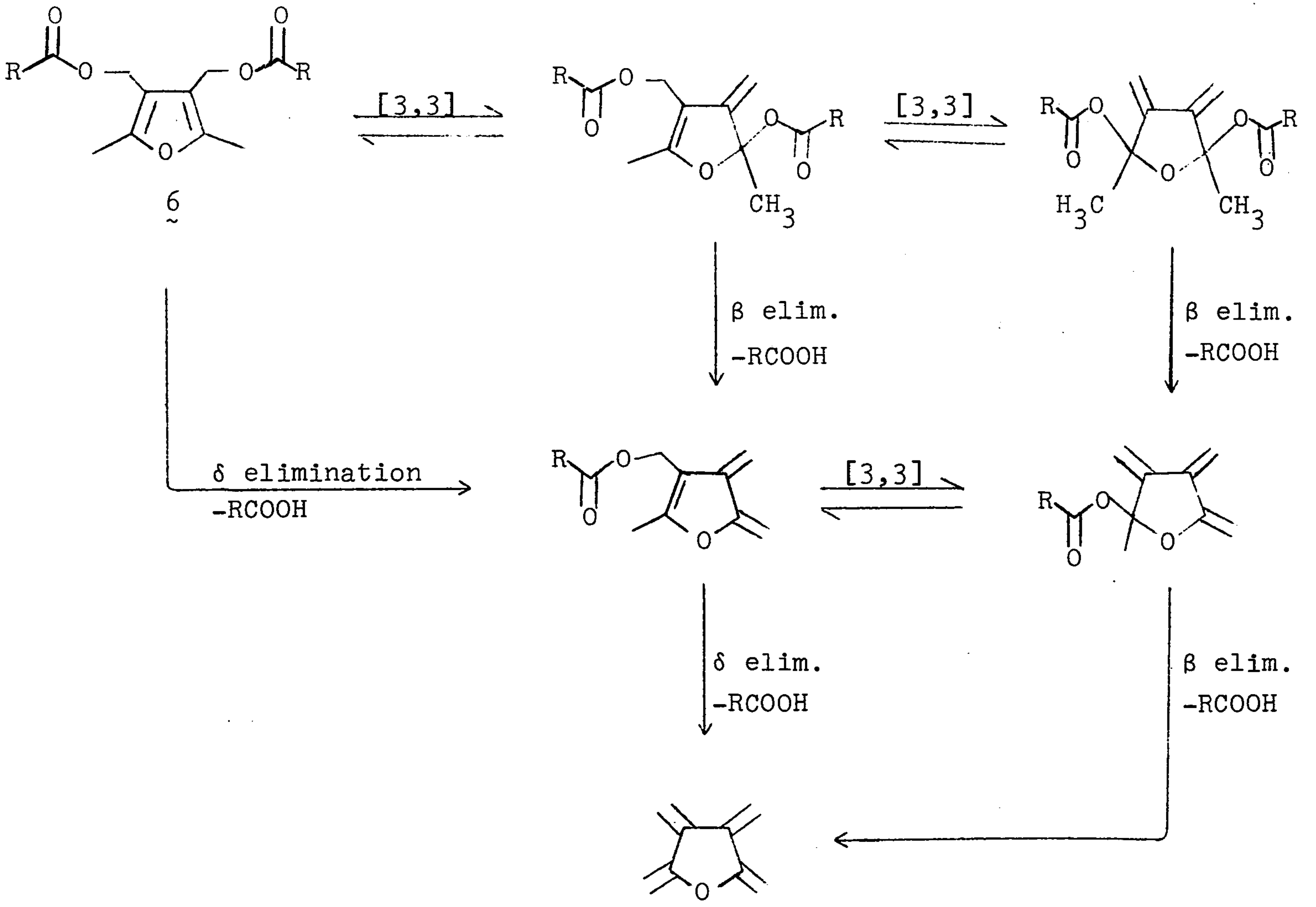

19

DISCUSSION

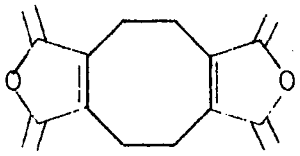
A migration mechanism was previously proposed for the conversion of 2-methyl-3-furylmethyl benzoate (**1**) to 2,3-dimethylene-2,3-dihydrofuran (**2**).[1] A set of mechanistic pathways which account for the formation of furanoradialene (**8**) from diesters (**6**) of 3,4-bis(hydroxymethyl)-2,5-dimethylfuran (**7**) are presented in Figure 3. Furanoradialene (**8**) may be formed either from diacetate **10** or dibenzoate **11** by two independent β eliminations of the corresponding carboxylic acid, after a [3,3] shift of the carboxylate group. This type of 1,4 elimination of a carboxylic acid during ester pyrolysis has literature precedent in the pyrolysis of allylic[45-50] and benzylic [51-53] esters containing δ hydrogens. In the product mixtures from several allylic esters, the initially formed [3,3] shift products have been isolated.[45,49,54-60]

A less likely explanation for the formation of furanoradialene (**8**) from **6** involves direct δ eliminations of two molecules of the corresponding carboxylic acid from **6** to form **8**. Although the δ-elimination pathway can not be ruled out, there are no literature examples of 1,4 eliminations during ester pyrolyses in which the two-step mechanism, involving a [3,3] shift of the carboxylate group, followed by β elimination of the carboxylic acid, can not explain the experimental results.

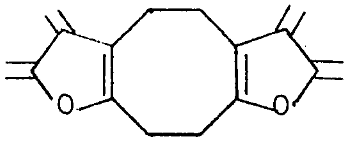
Figure 3. Mechanistic scheme for the formation of furanoradialene (**8**) from diesters (**6**) of 3,4-bis(hydroxymethyl)-2,5-dimethylfuran (**7**)


6
[3,3]
[3,3]
CH3
H3C
CH3
β elim.
-RCOOH
β elim.
-RCOOH
δ elimination
-RCOOH
[3,3]
δ elim.
-RCOOH
β elim.
-RCOOH

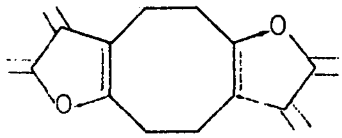
The exclusive formation of [4+2] dimer 12 can be explained by a concerted, Diels-Alder dimerization of furanoradialene (8). An alternative diradical pathway for the dimerization of 8 should lead to the formation of one or more of the possible [4+4] dimers (22-25) in addition to [4+2] dimer 12.



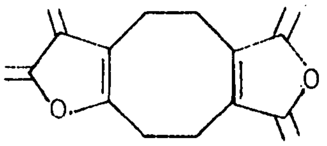
22



23

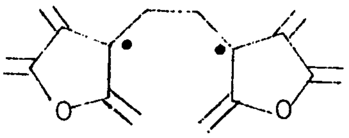


24

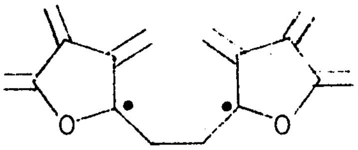


25

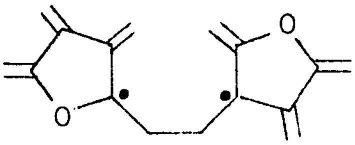
There are three possible diradical intermediates from 8: 26, 27 and 28. Intermediate 26 is the only diradical intermediate which can form the observed [4+2] dimer 12 and would be expected to form one or more of the [4+4] dimers (22, 23 or 25) as minor products. Since [4+2] dimer 12 is the only dimer of 8 detected in the product mixture using ^{1}H and ^{13}C NMR techniques, the diradical pathway is assumed to be less likely than the concerted pathway.



26

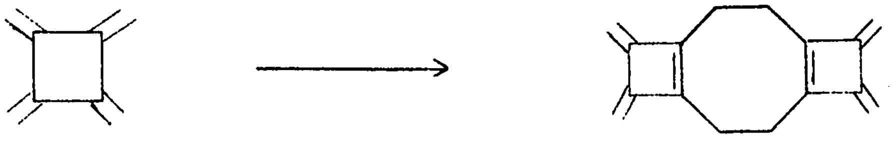


27



28

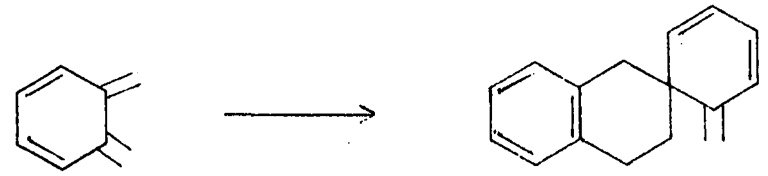
In the analogous dimerization of [4] radialene 29, the only product isolated was [4+4] dimer 30 and a diradical mechanism was proposed for its formation.[19-21]



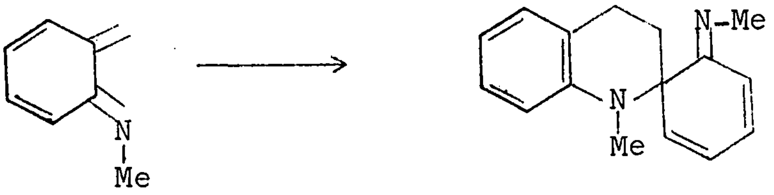
29

30

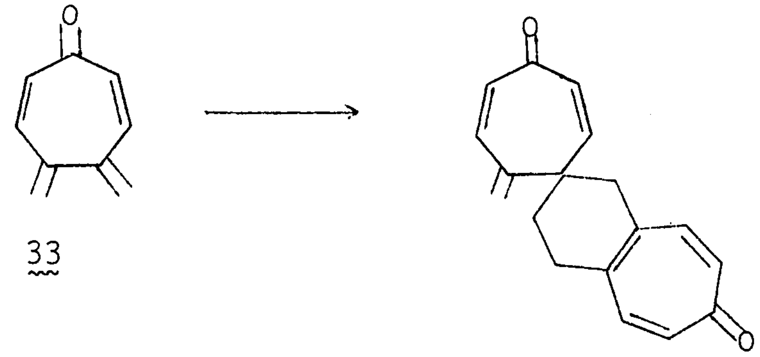
The formation of [4+2] dimer 12 has literature precedent in the formation of spirodimers from *ortho*-xylylene (31),[61] imine (32),[62] and 4,5-bis(methylene)cyclohepta-2,6-dien-1-one (33).[63]



31



32



33

EXPERIMENTAL

Methods and Materials. The pyrolysis apparatus has been previously described.[64] ^1H NMR spectra were recorded on Varian EM-360, Varian HA-100, Hitachi-Perkin Elmer R-20B, JEOL FX-90Q or Bruker WM-300 spectrometers. ^{13}C NMR spectra were recorded using a JEOL FX-90Q spectrometer. Chemical shifts are recorded in parts per million (δ) from tetramethylsilane (Me_4Si). Infrared spectra were measured with a Beckman 4250 spectrophotometer. High resolution mass spectra were measured with an Associated Electronics Industries MS-902 instrument at 70 eV. Gas chromatography (GLC) analyses were performed using a Hewlett Packard HP 5840A instrument with a 25 meter, fused-silica, capillary column coated with a methyl silicone liquid phase. Melting points were determined with a Thomas-Hoover apparatus and are uncorrected.

Dimethyl acetylenedicarboxylate and methyl acrylate were obtained from Aldrich Chemical Co. Lithium aluminum hydride, lithium aluminum deuteride and sodium hydride were obtained from Alfa Products. Acetyl chloride, benzoyl chloride and triethylamine were obtained from Eastman Organic Chemicals. Ethyl acetoacetate and iodine were obtained from Fisher Scientific Co. Sulfur dioxide was obtained from Matheson Gas Products.

Diethyl 2,5-Dimethyl-3,4-furandicarboxylate (9). To a mechanically stirred slurry of 24.52 g (1.0 mole) of sodium hydride (49.05 g of a 50% dispersion in mineral oil which was washed five times with 100 mL of pentane) in 700 mL of dry ether ($LiAlH_4$) at 0°C, was slowly added a solution of 130 g (1.0 mole) of freshly distilled ethyl acetoacetate in 300 mL of dry ether (dropwise addition over a 2 h period). Ether was added when necessary to facilitate stirring (ca. 700 mL total). After stirring the mixture for 1 h at 0°C, a suspension of 127 g (0.5 mole) of finely-powdered iodine in ether was added over a 2 h period. The mixture was stirred overnight at room temperature (ca. 11 h) and then the sodium iodide precipitate was separated by suction filtration and washed with several portions of ether. After removal of the solvent by distillation, 82.94 g (0.321 mole; 64%) of diethyl 2,3-diacetylsuccinate[65,42] was isolated. Without purification, this material was converted to diethyl 2,5-dimethyl-3,4-furandicarboxylate (9) using a literature method.[41,42] Diethyl 2,3-diacetylsuccinate (82.94 g; 0.321 mole) was dissolved in 300 mL of cold, concentrated sulfuric acid. After stirring for 3 h at 0°C, the mixture was poured over cracked ice in a 1 L beaker. After the ice had melted, the layers were separated and the aqueous layer was extracted with ether (8 x 100 mL). The combined ether and organic layers were washed with saturated sodium bicarbonate (5 x 100 mL) and saturated sodium chloride (3 x 100 mL). After drying ($MgSO_4$) and removal of the solvent, the crude product (67.85 g; 0.282 mole; 88%) was purified by vacuum distillation yielding 50.277 g [0.209 mole; 65.2% (42% isolated yield from ethyl acetoacetate)] of 9: bp 84-85°C (0.01 mm) [lit.[42] bp 127-130°C (1.0 mm)]; IR (thin film) 1720, 1640, 1590, 1420, 1205, 1080, 1025, 775 cm^{-1} [lit.[42] IR (thin film) 1724 cm^{-1}]; ^1H NMR ($CDCl_3$) δ 4.28 (q, J = 7 Hz, 4H), 2.42 (s, 6H), 1.33 (t, J = 7 Hz, 6H) [lit.[42] ^1H NMR (CCl_4) δ 4.28 (q, 4H), 2.44 (s, 6H), 1.32 (t, 6H)]; ^{13}C NMR ($CDCl_3$) δ 163.14, 155.07, 113.68, 60.16, 13.90, 12.60; high resolution mass spectrum calcd for $C_{12}H_{16}O_5$ 240.09978, measured 240.09957.

3,4-Bis(hydroxymethyl)-2,5-dimethylfuran (7). To a stirred slurry of 5.23 g (0.138 mole) of lithium aluminum hydride in 250 mL of dry ether ($LiAlH_4$) at 0°C, was slowly added a solution of 16.139 g (0.0672 mole) of diethyl 2,5-dimethyl-3,4-furandicarboxylate (9) in 100 mL of dry ether. After stirring the mixture for 4 h at room temperature, a standard workup[66] yielded 10.18 g (0.0651 mole; 97%) of crude product. Recrystallization from ether yielded

9.64 g (0.0617 mole; 92%) of 7: IR ($CHCl_3$) 3610, 3395, 1612, 1163, 1095, 996 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.38, (s, 4H), 3.89 (broad s, 2H), 2.20 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 146.67 (s), 118.77 (s), 54.96 (t, J = 143 Hz), 11.13 (q, J = 128 Hz).

3,4-Bis(acetoxymethyl)-2,5-dimethylfuran (10). A solution of 2.36 g (0.03 mole) of acetyl chloride in 20 mL of dry ether ($LiAlH_4$) was added dropwise to a stirred solution of 1.214 g (0.0078 mole) of 3,4-bis(hydroxymethyl)-2,5-dimethylfuran (7) and 1.97 g (0.019 mole) of triethylamine in 50 mL of dry ether. After the mixture was stirred for 8 h at room temperature, 10 mL of water was added and the layers were separated. The aqueous layer was extracted with ether (5 x 10 mL). The combined ether layers were washed with 1M hydrochloric acid (3 x 10 mL), saturated sodium bicarbonate (3 x 10 mL) and saturated sodium chloride (3 x 10 mL). After drying ($MgSO_4$) and removal of the solvent, the crude product was purified by distillation yielding 1.813 g (0.0076 mole; 97%) of 10: bp 94°C (0.05 mm); IR (thin film) 1740, 1606, 1225, 1166, 1015, 954, 762 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.92 (s, 4H), 2.28 (s, 6H), 2.06 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 170.70 (s), 149.52 (s), 114.80 (s), 56.83 (t, J = 148 Hz), 20.86 (q, J = 129 Hz), 11.43 (q, J = 128 Hz); high resolution mass spectrum calcd for $C_{12}H_{16}O_5$ 240.09978, measured 240.100439.

3,4-Bis(benzoyloxymethyl)-2,5-dimethylfuran (11). A solution of 30.64 g (0.218 mole) of benzoyl chloride in 50 mL dry ether ($LiAlH_4$) was added dropwise to a stirred solution of 15.47 g (0.0991 mole) of 3,4-bis(hydroxymethyl)-2,5-dimethylfuran (7) and 31.672 g (0.313 mole) of triethylamine in 400 mL of dry ether. After the mixture was stirred for 7 h at room temperature, 50 mL of water was added and the layers were separated. The aqueous layer was extracted with ether (4 x 25 mL). The combined ether layers were washed successively with 1 M hydrochloric acid (3 x 30 mL), saturated sodium bicarbonate (4 x 25 mL) and saturated sodium chloride (3 x 25 mL). After drying ($MgSO_4$) and removal of the solvent, the crude product (32.846 g; 0.0901 mole; 91%) was purified by recrystallization from ether yielding 25.938 g (0.0712 mole; 72%) of clear prisms of 11: mp 97-97.8°C; IR ($CHCl_3$) 1720, 1622, 1265, 1170, 1100, 1020, 915, 865, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.14-7.8 (m, 4H), 7.65-7.03 (m, 6H), 5.24 (s, 4H), 2.33 (s, 6H); high resolution mass spectrum calcd for $C_{22}H_{20}O_5$ 364.13108, measured 364.13145.

General Pyrolysis Procedure. The pyrolyses were run at temperatures from 450 to 650°C. A sample of the furylmethyl ester in a Pyrex boat was placed into the sample compartment and the apparatus was heated to obtain temperatures ranging from 50 to 150°C. A condenser cooled to ca. -20°C was inserted between the furnace and the liquid-nitrogen-cooled trap to collect any unreacted starting material and benzoic acid formed as a byproduct in the pyrolyses of dibenzoate 11. During each pyrolysis, 2 mL of a 1:1 mixture of carbon disulfide (CS_2) and deuterochloroform ($CDCl_3$) was deposited onto the trap through a side arm. After all of the starting material had distilled out of the sample compartment, nitrogen was introduced into the system and a weighed amount of 1,2-dichloroethane or 1,1,2,2-tetrachloroethane was added for use as an internal standard. The trap was then warmed to -78°C and a 1:1 mixture of CS_2 and $CDCl_3$ (2 mL) was used to rinse the material on the insert of the trap to the bottom. The product solution was mixed by rinsing the walls of the trap with the solution ca. ten times using a cold pipette (CS_2 at -78°C). The product solution was placed into four 5 mm NMR tubes at -78°C and NMR spectra were recorded at temperatures below -60°C for each tube. After the tubes were warmed to 0°C, NMR spectra were again recorded.

Pyrolysis of 3,4-Bis(acetoxymethyl)-2,5-dimethylfuran (10). A 0.3413 g quantity of 10 was pyrolyzed at 570°C using the general procedure. After the product solution was placed into the NMR tubes at -78°C, ^1H and ^{13}C NMR spectra were recorded at temperatures below -70°C. The tubes were slowly warmed to 0°C and NMR spectra were again recorded. The yields of furanoradialene (8) and [4+2] dimer 12 were determined by quantitative ^1H NMR analysis using known amounts of dichloroethane as an internal standard. In addition to products 8 and 12, a large amount of air-sensitive, cellophane-like polymer was deposited in the area of the apparatus from the furnace to the liquid-nitrogen-cooled trap. At a pyrolysis temperature of 570°C, a 13% yield of furanoradialene (8) was detected in the NMR tubes at temperatures below -70°C, along with ca. 1% of [4+2] dimer 12. At 0°C, the product solution consisted of [4+2] dimer 12 (12% from 10: 91.3% from 8) and a small amount of white, insoluble, polymeric material. The products were identified from the following data.

*Furanoradialene (**8**), (2,3,4,5-tetrakis(methylene)-2,3,4,5-tetrahydrofuran):* ^{1}H NMR (1:1 $CS_2/CDCl_3$; -78°C) δ 5.55 (s, 2H), 5.52 (s, 2H), 4.59 (d, J = 3 Hz, 2H), 4.52 (d, J = 3 Hz, 2H); ^{13}C NMR (1:1 $CS_2/CDCl_3$; -78°C) δ 156.08 (s), 135.76 (s), 105.97 (t, J = 162 Hz), 81.86 (t, J = 162 Hz); [lit.[28] ^{1}H NMR ($CDCl_3$; -50°C) δ 5.59 (broad s, 4H), 4.61 (AB quartet, J = 2.5 Hz, 4H); ^{13}C NMR ($CDCl_3$; -60°C) δ 160.5, 156.6, 106.2, 81.8].

*[4+2] Dimer **12**:* ^{1}H NMR (1:1 $CS_2/CDCl_3$) δ 5.5 (s, 1H), 4.92 (s, 1H), 4.54 (d, J = 2.5 Hz, 1H), 4.46 (d, J = 2.5 Hz, 4H), 4.09 (m, 2H), 3.94 (d, J = 2.5 Hz, 1H), 2.55-2.27 (m, 4H), 1.88-1.65 (m, 2H); ^{13}C NMR (1:1 $CS_2/CDCl_3$) δ 165.72, 160.95, 160.79, 156.99, 146.76, 134.79, 133.76, 106.72, 82.62, 81.48, 81.05, 80.83, 45.02, 33.26, 30.23, 18.09.

*Pyrolysis of 3,4-Bis(benzoyloxymethyl)-2,5-dimethylfuran (**11**).* A 0.4394 g (1.21 mmol) quantity of **11** was pyrolyzed at 610°C using the general procedure. ^{1}H and ^{13}C NMR analyses at -70°C indicated that furanoradialene (**8**) and [4+2] dimer **12** were the only major products formed from **11**, aside from benzoic acid and a substantial amount of white, polymeric material. Quantitative ^{1}H NMR analysis at -78°C indicated that the product mixture consisted of 0.359 mmol of furanoradialene (**8**) (30%) and 0.211 mmol of [4+2] dimer **12** (35%). The ^{1}H and ^{13}C NMR spectra of **8** formed from dibenzoate **11** matched the spectra of **8** formed from diacetate **10**. For furanoradialene (**8**): ^{1}H NMR (1:1 $CS_2/CDCl_3$; -70°C) δ 5.58 (s, 2H), 5.55 (s, 2H), 4.62 (d, J = 2.5 Hz, 2H), 4.52 (d, J = 2.5 Hz, 2H); ^{13}C NMR (1:1 $CS_2/CDCl_3$; -70°C) δ 155.97, 135.76, 105.86, 81.86. Upon warming the samples above -50°C, **8** rapidly dimerized forming [4+2] dimer **12**: ^{1}H NMR (1:1 $CS_2/CDCl_3$; -30°C) δ 5.51 (s, 1H), 4.93 (s, 1H), 4.55 (d, J = 2.5 Hz, 1H), 4.46 (d, J = 2.5 Hz, 4H), 4.12 (m, 2H), 3.94 (d, J = 2.5 Hz, 1H), 2.58-2.23 (m, 4H), 1.86-1.64 (m, 2H),; ^{13}C NMR (1:1 $CS_2/CDCl_3$; -40°C) δ 165.02, 160.36, 160.25, 156.40, 146.05, 134.52, 133.49, 106.72, 82.56, 81.75, 81.32, 81.05, 44.59, 33.05, 29.69, 17.88. ^{1}H NMR analysis using a 1,1,2,2-tetrachloroethane internal standard indicated that a quantitative yield of [4+2] dimer **12** was formed from **8** (69% yield from dibenzoate **11**).

*3,4-Bis[(hydroxy)dideuteromethyl]-2,5-dimethylfuran (**7**-d_4).* To a stirred slurry of lithium aluminum deuteride (3.41 g; 81.2 mmol) in 5 mL of dry ether ($LiAlH_4$) at 0°C, was added dropwise a solution of 5.4892 g (22.8 mmol) of diethyl 2,5-dimethyl-3,4-furandicarboxylate (**9**) in 20 mL of dry ether. After the mixture was stirred for 7 h at room temperature, a standard workup[66] yielded 2.88 g (17.98 mmol; 79%) of 7-d$_4$: IR (CHCl$_3$) 3605, 3400, 2260-2050, 1612, 1276, 995, 860 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.75 (broad s, 2H), 2.18 (s, 6H).

3,4-Bis[(acetoxy)dideuteromethyl]-2,5-dimethylfuran (10-d$_4$). A solution of 1.5537 g (19.8 mmol) of acetyl chloride in 10 mL of dry ether was added dropwise over a 15 min period to a stirred solution of 2.88 g (17.98 mmol) of 7-d$_4$ and 2.5167 g (24.9 mmol) of triethylamine in 15 mL of dry ether. After the mixture was stirred for 20 h at room temperature, 10 mL of water was added and the layers were separated. The aqueous layer was extracted with ether (3 x 10 mL). The combined ether layers were washed successively with water (2 x 10 mL), 1 M hydrochloric acid (3 x 10 mL), saturated sodium bicarbonate (3 x 25 mL) and saturated sodium chloride (2 x 25 mL). After drying (MgSO$_4$) and removal of the solvent, the crude product (3.0676 g; 12.56 mmol; 70%) was purified by short-path distillation, yielding 2.5291 g (10.35 mmol; 58% isolated yield) of 10-d$_4$: bp 80-81°C (0.005 mm); IR (thin film) 2280-2040, 1735, 1610, 1255, 1155, 1045, 1015, 925 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.26 (s, 6H), 2.05 (s, 6H); ^{13}C NMR (CDCl$_3$) δ 170.92, 149.63, 114.52, 20.97, 11.48; high resolution mass spectrum calcd for $C_{12}H_{12}D_4O_5$ 244.12489, measured 244.12465. ^1H NMR spectral analysis of 10-d_4 showed no evidence for any deuterated species other than 10-d_4.

Pyrolysis of 3,4-Bis[(acetoxy)dideuteromethyl]-2,5-dimethylfuran (10-d_4). A 0.4216 g quantity of 10-d_4 was pyrolpyrolyzed at 600°C using the general procedure. The pyrolysate was collected in 4 mL of 1:1 $CS_2/CDCl_3$ and NMR spectral data were recorded at low temperature for 3,4-bis-(methylene-d_2)-2,5-dimethylene-2,3,4,5-tetrahydrofuran (8-d_4): ^1H NMR (1:1 $CS_2/CDCl_3$; -60°C) δ 4.61 (d, J = 2.5 Hz, 2H), 4.52 (d, J = 2.5 Hz, 2H); ^{13}C NMR (1:1 $CS_2/CDCl_3$; -60°C) δ 156.08, 135.60, 81.80. Upon warming the samples to room temperature, 8-d_4 was cleanly converted to [4+2] dimer 12-d_8: ^1H NMR (1:1 $CS_2/CDCl_3$) δ 4.53 (d, J = 2.5 Hz, 1H), 4.45 (d, J = 2.5 Hz, 4H), 4.09 (m, 2H), 3.92 (d, J = 2.5 Hz, 1H); ^{13}C NMR (1:1 $CS_2/CDCl_3$) δ 165.42, 160.64, 160.31, 156.57, 146.53, 134.65, 133.58, 82.51, 81.64, 81.21, 80.99, 44.89. The signals for the CD_2 carbons were not observed after 25,000 scans (pulse width = 2.0 μs). NMR analysis of the pyrolysis product mixtures formed from 10-d_4 showed no evidence for any deuterated species other than 8-d_4 and 12-d_8.

Diels-Alder Reaction of 8 with a Large Excess of Methyl Acrylate (13). A 0.1368 g (0.5694 mmol) quantity of diacetate 10 was pyrolyzed at 590°C and 10^{-4} Torr. During the pyrolysis, a solution of 9.4779 g (110 mmol; 97 equivalents) of methyl acrylate in 10 mL of CS_2 was deposited into the trap via a side arm. After the apparatus was shut down under nitrogen, the trap was warmed to -78°C (dry ice/isopropanol) and 10 mL of CS_2 were used to rinse the material on the walls of the trap to the bottom. The product solution was stirred at temperatures below -72°C for 12 h and then was warmed to -20°C. After 4 h at -20°C, the product solution was warmed to room temperature. After drying (Na_2CO_3) and removal of the solvent with a rotary evaporater, spectral analyses indicated that the product mixture consisted of a diadduct 15 of furanoradialene (8) with methyl acrylate (13), along with smaller amounts of [4+2] dimer 12 and a Diels-Alder adduct 16 of 12 with methyl acrylate. Diadduct 15 showed the following spectral data: IR ($CHCl_3$) 1730, 1612, 1450, 1285, 1085, 1062 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.8-3.65 (overlapping singlets, 6H), 3.0-0.7 (m, 14H). The existence of the Diels-Alder adduct 16 of [4+2] dimer 12 and methyl acrylate 13 was inferred from the integration of the ^1H NMR signals, which indicated that part of the 2,3-dimethylene moiety in 12 had reacted. Attempts to isolate products 15 and 16 by liquid chromatography (both TLC and column) were unsuccessful due to decomposition of 12 and 16 on the column and rapid elution of the decomposition products.

Attempted Diels-Alder Reaction of Furanoradialene (8) with Dimethyl Acetylenedicarboxylate (14). A 0.4000 g (1.098 mmol) quantity of dibenzoate 11 was pyrolyzed at 630°C and 10^{-4} Torr. During the pyrolysis, 1.48 g (10.4 mmol; 9.5 equivalents) of dimethyl acetylenedicarboxylate (14) and 1.5 mL of carbon disulfide were distilled into the product trap via a side arm. In order to distil the dibenzoate (11) into the hot zone, the sample compartment was heated to ca. 140°C. After the apparatus was shut down under nitrogen, 0.0280 g (0.167 mmol) of 1,1,2,2-tetrachloroethane was added as an internal standard. The trap was warmed to -78°C and 2.5 mL of a 3:2 mixture of $CDCl_3$ and CS_2 at -78°C was used to rinse the material on the walls of the trap to the bottom. The product solution was placed into four 5 mm NMR tubes at -78°C and ^1H NMR spectra were recorded for each tube at -80°C. At -80°C, the product mixture consisted mainly of furanoradialene (8) along with minor amounts of [4+2] dimer 12.

One of the tubes was warmed first to -30°C and then to 0°C and a ^{1}H NMR spectrum was recorded at each temperature. All of the furanoradialene (**8**) was converted into [4+2] dimer **12**. The remaining tubes were maintained at temperatures below -60°C for 60 h. During the 60 h time period, almost all of the furanoradialene (**8**) was converted into [4+2] dimer **12**. There was no ^{1}H NMR evidence for the formation of either a Diels-Alder monoadduct or a diadduct of furanoradialene (**8**) with dimethyl acetylenedicarboxylate (**14**).

*Attempted Chelatropic Reaction of **8** with Sulfur Dioxide.* A 0.4128 g quantity of dibenzoate **11** was pyrolyzed at 640°C and 10^{-4} Torr. During the pyrolysis, 2 mL of dichloromethane-$\underline{d}_2$ was deposited into the trap via a side arm. After all of the dibenzoate **11** had distilled out of the sample compartment (heating from 86 to 140°C), the apparatus was shut down under nitrogen. The product trap was then warmed to -78°C and 2 mL of CD_2Cl_2 was used to rinse the material on the walls of the trap to the bottom. Excess sulfur dioxide (SO_2) was slowly condensed into the trap and the resulting yellow mixture, containing a large amount of insoluble, polymeric material, was maintained at -78°C for 1 h. After removing most of the excess sulfur dioxide by distillation toward a liquid-nitrogen-cooled trap, the product solution was placed into three, 5 mm NMR tubes. Attempts to record ^{1}H NMR spectra of this product solution at -60°C were unsuccessful because the concentration of products was too small to obtain meaningful spectra. The cold product solution was then added to 60 mL of pentane at room temperature and a yellow, labile sold immediately precipitated. Collection of the solid by suction filtration under nitrogen yielded diadduct 17: IR ($CHCl_3$) 1330, 1110 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 4.42 (m, 4H), 4.32 (m, 4H). Polymeric material was the major product and under no conditions used was the diadduct formed in greater than 10% yield. No ^{1}H NMR evidence for the formation of either [4+2] dimer 12 or a monoadduct (20 or 21) of furanoradialene (8) with SO_2 was observed. The large amount of polymer formed in each experiment may be partially due to decomposition of 12, 20, or 21 under the reaction conditions. Attempts to separate the products by liquid chromatography (TLC and column) resulted in complete decomposition of the product mixtures.

REFERENCES

1. Trahanovsky, W. S.; Cassady, T. J.; Woods, T. L. *J. Am. Chem. Soc.* 1981, 103, 6691.
2. Winberg, H. E.; Fawcett, F. S.; Mochel, W. E.; Theobald, C. W. *J. Am. Chem. Soc.* 1960, 82, 1428.
3. Jullien, J.; Pechine, J. M.; Perez, F.; Piade, J. J. *Tetrahedron Lett.* 1979, 3079.
4. Hart, H.; Teuerstein, A.; Jeffares, M.; Kung, W.-J. H.; Ward, D. L. *J. Org. Chem.* 1980, 45, 3731.
5. Waitkus, P. A.; Peterson, L. I.; Griffin, G. W. *J. Am. Chem. Soc.* 1966, 88, 181.
6. Waitkus, P. A.; Sanders, E. B.; Peterson, L. I.; Griffin, G. W. *J. Am. Chem. Soc.* 1967, 89, 6318.
7. Dorko, E. A.; *J. Am. Chem. Soc.* 1965, 87, 5518.
8. Laseter, J. L.; Manmade, A.; Waitkus, P. A.; Griffin, G. W. *Spectrochim. Acta. Part A* 1971, 27, 741.
9. Mandel'shtam, T. V.; Kharicheva, E. M. *Zh. Org. Chem.* 1973, 9, 1648.
10. Dorko, E. A.; Scheps, R.; Rice, S. A. *J. Phys. Chem.* 1974, 78, 568.
11. Rhee, K. H.; Miller, F. A. *Spectrochim. Acta, Part A* 1971, 27, 1.
12. Dorko, E. A.; Hencher, J. L.; Bauer, S. H. *Tetrahedron* 1968, 24, 2425.
13. Burr, J. C., Jr.; Dorko, E. A.; Merritt, J. A. *J. Chem. Phys.* 1966, 45, 3877.
14. Bally, T.; Haselbach, E.; Lanyiova, Z.; Baertschi, P. *Helv. Chim. Acta* 1978, 61, 2488.
15. Bally, T.; Haselbach, E. *Helv. Chim. Acta* 1978, 61, 754.

16. Bally, T.; Baumgartel, H.; Buchler, U.; Haselbach, E.; Lohr, W.; Maier, J. P.; Vogt, J. Helv. Chim. Acta 1978, 61, 741.

17. Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. Helv. Chim. Acta 1977, 60, 2213.

18. Bally, T.; Haselbach, E. Helv. Chim. Acta 1975, 58, 321.

19. Griffin, G. W.; Peterson, L. I. J. Am. Chem. Soc. 1962, 84, 3398.

20. Griffin, G. W.; Peterson, L. I. J. Am. Chem. Soc. 1963, 85, 2268.

21. Trabert, L.; Hopf, H. Liebigs Ann. Chem. 1980, 1786.

22. Miller, F. A. Appl. Spectrosc. 1975, 29, 461.

23. Miller, F. A.; Brown, F. R.; Rhee, K. H. Spectrochim. Acta, Part A 1972, 28, 1467.

24. Bally, T.; Buser, U.; Haselbach, E. Helv. Chim. Acta 1978, 61, 38.

25. Barkovich, A. J.; Strauss, E. S.; Vollhardt, K. P. C. J. Am. Chem. Soc. 1977, 99, 8321.

26. Harruff, L. G.; Brown, M.; Boekelheide, V. J. Am. Chem. Soc. 1978, 100, 2893.

27. Schiess, P.; Heitzmann, M. Helv. Chim. Acta 1978, 61, 844.

28. Jullien, J.; Pechine, J. M.; Perez, F.; Piade, J. J. Tetrahedron Lett. 1980, 21, 611.

29. Kobrich, G.; Heinemann, H. Angew. Chem. Intl. Ed. Eng. 1965, 4, 594.

30. Kobrich, G.; Heinemann, H.; Zundorf, W. Tetrahedron. 1967, 23, 565.

31. Gerson, F.; Heilbronner, E.; Kobrich, G. Helv. Chem. Acta 1965, 48, 1525.

32. Uhler, R. O.; Shechter, H.; Tiers, G. V. D. J. Am. Chem. Soc. 1962, 84, 3397.

33. Weltin, E.; Gerson, F.; Murrell, J. N.; Heilbronner, E. Helv. Chim. Acta 1961, 44, 1400.

34. Hopff, H.; Wick, A. K. Helv. Chim. Acta 1961, 44, 380.

35. Hopff, H.; Gati, A. Helv. Chim. Acta 1965, 48, 1289.

36. Gerson, F. Helv. Chim. Acta 1964, 47, 1941.

37. Marsh, W.; Dunitz, J. D. Helv. Chim. Acta 1975, 58, 707.

38. Hart, H.; Sasaoka, M. J. Am. Chem. Soc. 1978, 100, 4326.

39. Gall, J. H.; Gilmore, C. J.; MacNicol, D. D. Chem. Commun. 1979, 927.

40. Ando, W.; Haniu, Y.; Takata, T. Tetrahedron Lett. 1981 22, 4815.

41. Knorr, L. Chem. Ber. 1884, 17, 2863.

42. Newman, M. S.; Cella, J. A. J. Org. Chem. 1973, 38, 3482.

43. Pouchert, C. "The Aldrich Library of Infrared Spectra", 2nd ed.; Aldrich Chemical Co. Inc.: Milwaukee, 1975; Vol. II, p 471F.

44. Trahanovsky, W. S.; Cassady, T. J.; Unpublished Results.

45. Bailey, W. J.; Barclay, R., Jr. J. Org. Chem. 1956, 21, 328.

46. Grummitt, O.; Splitter, J. J. Am. Chem. Soc. 1952, 74, 3924.

47. Grummitt, O.; Mandel, Z. J. Am. Chem. Soc. 1956, 78, 1054.

48. Bailey, W. J.; Goossens, J. C. J. Am. Chem. Soc. 1956, 78, 2804.

49. a) Greenwood, F. L. J. Org. Chem. 1959, 24, 1735.

b) Greenwood, F. L. J. Org. Chem. 1962, 27, 2308.

50. Clauson-Kaas, N.; Elming, N. Acta Chem. Scand. 1952, 6, 560.

51. Trahanovsky, W. S.; Morello, M. J. "Abstracts of Papers", 178th National Meeting of the American Chemical Society, Washington, D.C., Sept. 1979, American Chemical Society: Washington, D.C., 1979; PETR 46.

52. Morello, M. J. M.S. Thesis, Iowa State University, Ames, Iowa, 1980.

53. Cristol, S. J.; Barasch, W.; Tieman, C. H. J. Am. Chem. Soc. 1955, 77, 583.

54. Marvel, C. S.; Brace, N. O. J. Am. Chem. Soc. 1948, 70, 1775.

55. Landor, P. D.; Landor, S. R. J. Chem. Soc. 1956, 1015.

56. Heilbron, I. M.; Jones, E. R. H.; McCombie, J. T.; Weedon, B. C. J. Chem. Soc. 1945, 88.

57. Burton, H. J. Chem. Soc. 1928, 1650.

58. Balfe, M. P.; Kenyon, J. Trans. Faraday Soc. 1941, 37, 721.

59. Braude, E. A.; Turner, D. W.; Waight, E. S. J. Chem. Soc. 1958, 2396.

60. Braude, E. A.; Turner, D. W. J. Chem. Soc. 1958, 2404.

61. Errede, L. A. J. Am. Chem. Soc. 1961, 83, 949.

62. Ito, Y.; Miyata, S.; Nakatsuka, M.; Saegusa, T. J. Am. Chem. Soc. 1981, 103, 5250.

63. Lokensgard, D. M. Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1978.

64. Trahanovsky, W. S.; Ong, C. C.; Pataky, J. G.; Weitl, F. L.; Mullen, P. W.; Clardy, J. C.; Hansen, R. S. J. Org. Chem. 1971, 36, 3575.

65. Gardner, J. A.; Rydon, H. N. J. Chem. Soc. 1938, 45.

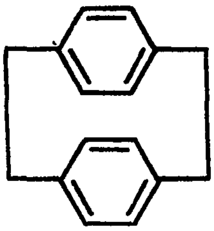
66. Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. I, p 584.

SECTION VI. SYNTHETIC APPROACHES TOWARD $[2_4](2,3,4,5)$-FURANOPHANE

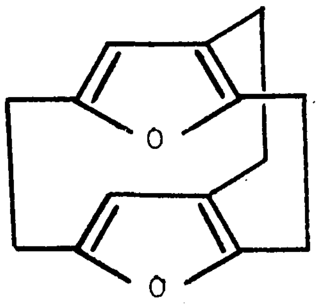
INTRODUCTION

The synthesis and study of the chemical and physical properties of bridged aromatic compounds, called cyclophanes,[1] has been an intensively investigated research area in recent years.[2-10] Cyclophanes are rigid molecules of known geometry which have been of interest because of the strain energy, bonding situation and transannular interactions which result from having two closely situated π-electron systems.

The cyclophane nomenclature, first introduced by Cram and Steinberg[1] and later extended by Vögtle and Neumann,[11] defines a cyclophane as a molecule having at least one bridged aromatic ring. The number of bridging atoms is given in brackets and is followed by parentheses containing designations for the positions of attachment on the aromatic ring. After the parentheses, the name of the aromatic ring is listed, followed by the suffix "-ophane". The parent term, cyclophane, refers to bridged benzene rings. Bridged heteroaromatic rings are called heterophanes. Thus, structure 1 is named [2.2](1,4)cyclophane, while structure 2 is named [2.2.2](2,3,5)furanophane. In naming multibridged cyclophanes in which all of the bridges contain the same number of atoms, the numbering can be simplified by using a subscript number to refer to the number of bridges.[11]

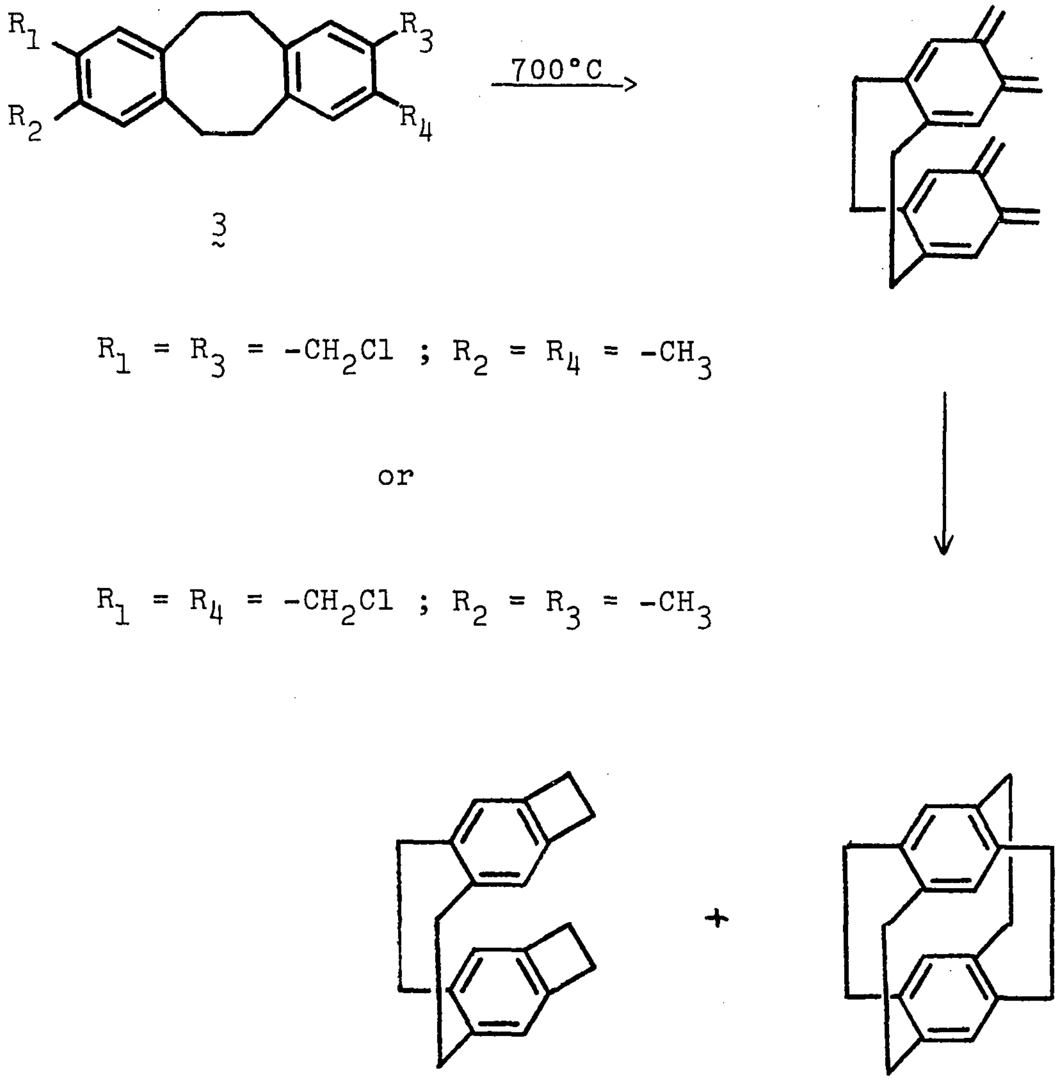


1



2

The availability of multibridged $[2_n]$cyclophanes has been dramatically increased in recent years by the work of Boekelheide, which has shown that two bridges at a time can be introduced into a cyclophane molecule by the reaction of properly situated *ortho*-xylylene moieties.[2] For example, pyrolysis of 3 at 700°C gave a mixture of 4 and $[2_4]$(1,2,4,5)cyclophane (5). Pyrolysis of 4 under the same conditions also leads to the formation of 5.[12] The basis for this work was the observation by Cava and Deana[13] that the pyrolysis of sulfone 6 produced [2.2](1,2)cyclophane (7) in good yield, presumably via the intermediacy of *ortho*-xylylene (8). Since the concerted dimerization of 8 to give 7 is "symmetry forbidden", according to the rules governing the conservation of orbital symmetry,[14] a diradical mechanism was proposed for the formation of 7. Boekelheide utilized reactions involving pyrolytic eliminations of hydrogen



3

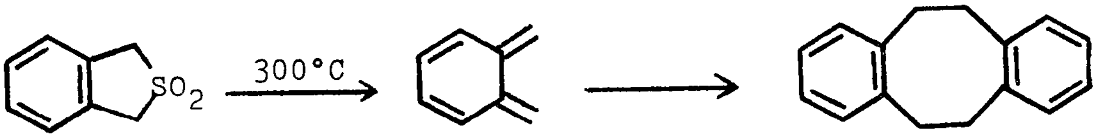
$R_1 = R_3 = -CH_2Cl$; $R_2 = R_4 = -CH_3$

or

$R_1 = R_4 = -CH_2Cl$; $R_2 = R_3 = -CH_3$

4 (26%)

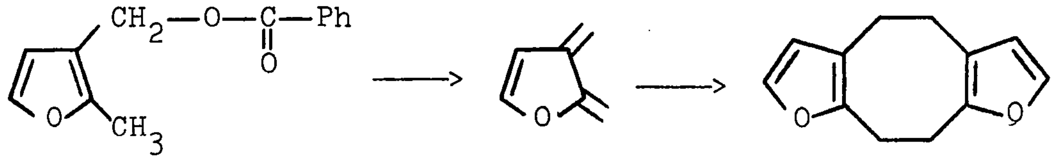
5 (17%)



6 8 7

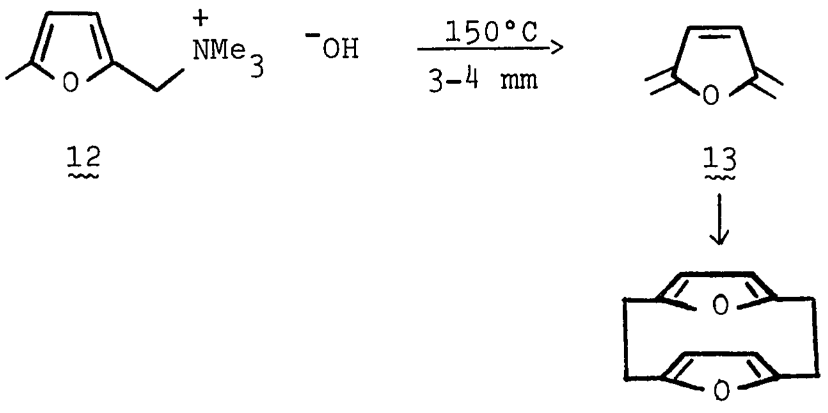
chloride from suitably substituted, *ortho*-methylbenzyl chlorides[15-22] or pyrolytic, ring openings of substituted benzocyclobutenes[23] to generate the necessary *ortho*-xylylene intermediates. This synthetic strategy was successfully employed in preparations of $[2_3]$(1,2,4)cyclophane,[24,25] $[2_3]$(1,2,3)cyclophane,[2] $[2_4]$(1,2,4,5)cyclophane,[12] $[2_4]$(1,2,3,4)cyclophane,[26,27] $[2_5]$(1,2,3,4,5)cyclophane,[28] and $[2_6]$(1,2,3,4,5,6)cyclophane which has also been referred to by the trivial name superphane.[26,29]

Recently we reported that the flash vacuum pyrolysis (FVP) of 2-methyl-3-furylmethyl benzoate (9) gives good yields of 2,3-dimethylene-2,3-dihydrofuran (10).[30] Compound 10 readily undergoes dimerization at temperatures above -30°C forming [2.2](2,3)furanophane (11). Based on the success of Boekelheide's syntheses of multibridged $[2_n]$-cyclophanes from *ortho*-xylylene intermediates and the facile, analogous dimerization of 2,3-dimethylene-2,3-dihydrofuran (10), a program aimed at the synthesis of multibridged $[2_n]$furanophanes was initiated.



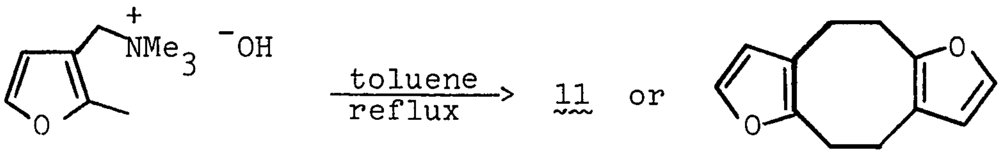
9   10   11

The first reported synthesis of a furanophane utilized a 1,6-elimination reaction from (5-methylfurfuryl)trimethylammonium hydroxide (12), forming 2,5-dimethylene-2,5-dihydrofuran (13).[31] Warming 13 in the presence of polymerization inhibitors led to dimerization, forming [2.2]-(2,5)furanophane (14) in high yield. The authors also reported that the liquid-phase pyrolysis of (2-methyl-3-furylmethyl)trimethylammonium hydroxide (15) formed either [2.2]-(2,3)furanophane (11) or [2.2](2,3)(3',2')furanophane (16) in 53% yield.



12   13

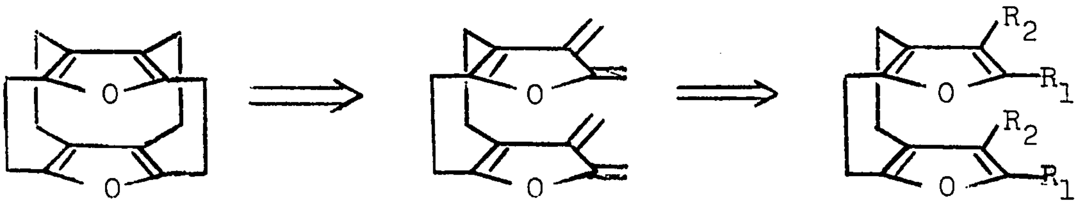
14 (72%)



15 16

The synthesis of several other [2.2]heterophanes using the Hoffman elimination approach have been reported.[32-46] In addition to these reports, Boekelheide synthesized two tetra-bridged pyridinophanes using pyrolytic eliminations of hydrogen chloride to generate the necessary *ortho*-quinodimethane intermediates.[47]

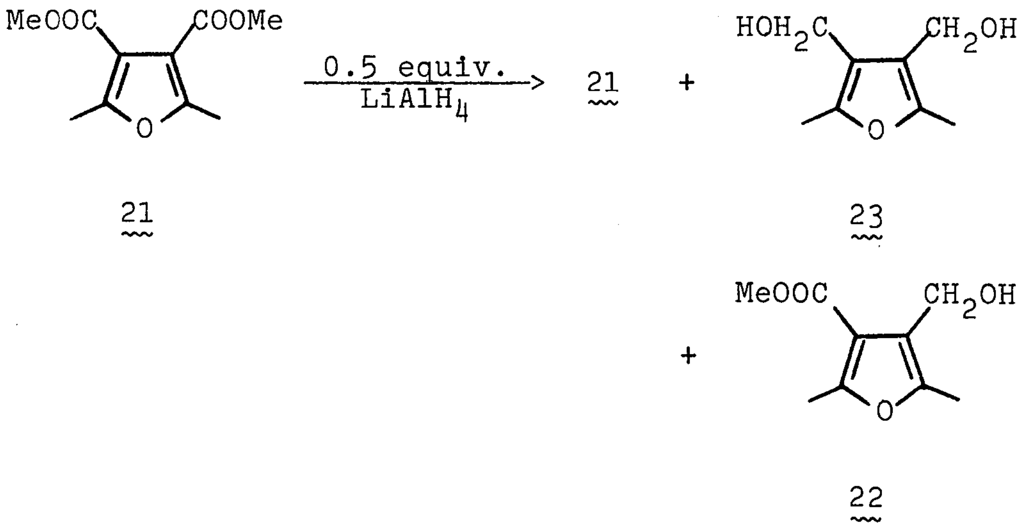
The synthetic strategy devised for the preparation of [2_4](2,3,4,5)furanophane (17) involved the generation of a molecule (18) containing two suitably positioned, 2,3-dimethylene-2,3-dihydrofuran units. The initial target molecule in the synthesis of 17 was a [2.2](2,3)furanophane molecule 19 containing functional groups necessary for the conversion of 19 into 18.

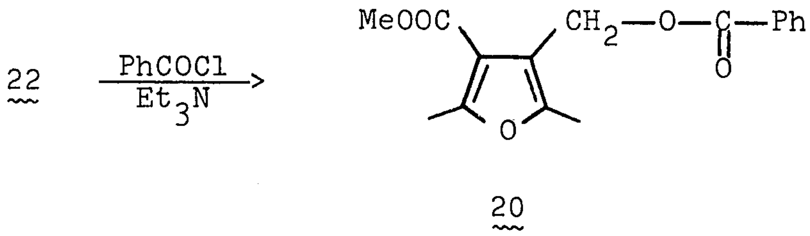


17 18 19

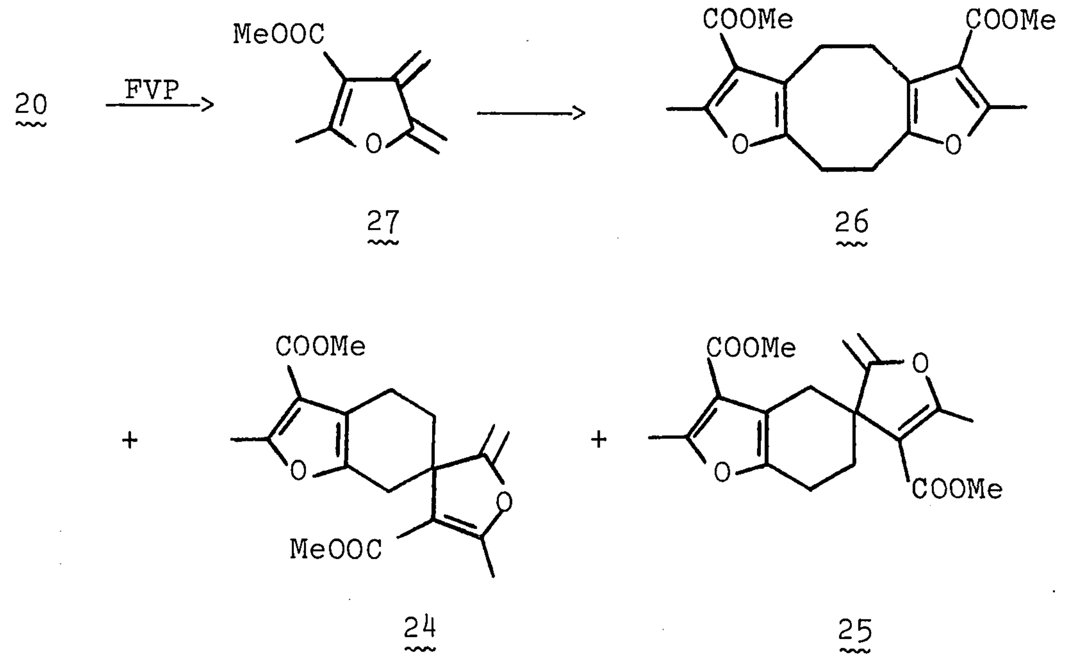
RESULTS

The emphasis of the initial experiments directed toward the total synthesis of [2_4](2,3,4,5)furanophane (17) was placed on developing an efficient route for the preparation of an initial target molecule with general structure 19. Since the pyrolytic elimination of benzoic acid from 2-methyl-3-furylmethyl benzoate is the best method currently available for the production of 2,3-dimethylene-2,3-dihydrofuran (10),[30] the preparation and study of the pyrolysis chemistry of 4-carbomethoxy-2,5-dimethyl-3-furylmethyl benzoate (20) was undertaken. Exposure of a sample of dimethyl 2,5-dimethylfuran-3,4-dicarboxylate (21) in ether to an amount of lithium aluminum hydride ($LiAlH_4$) equal to two hydride ions per molecule of 21, resulted in the formation of 4-carbomethoxy-2,5-dimethyl-3-furylmethyl alcohol (22) and 3,4-bis(hydroxymethyl)-2,5-dimethylfuran (23), in addition to the recovery of unreacted starting material 21. After the three major components of the product mixture were separated by column chromatography, 22 was converted to benzoate 20 by reaction with benzoyl chloride in the presence of triethylamine.





The FVP of 20 at temperatures ranging from 550 to 610°C and a pressure of approximately 10^{-4} Torr produced a white product band in the liquid-nitrogen-cooled trap. The product mixtures were dissolved in carbon disulfide at -78°C and then slowly warmed to 0°C. Under all pyrolysis and workup conditions, the major product isolated was a colorless, transparent polymer. In addition to the polymeric material, smaller amounts of [4+2] dimers 24 and 25 and head-to-head, [4+4] dimer 26 of 2,3-bis(methylene)-4-carbomethoxy-2,3-dihydro-4-methylfuran (27) were isolated.

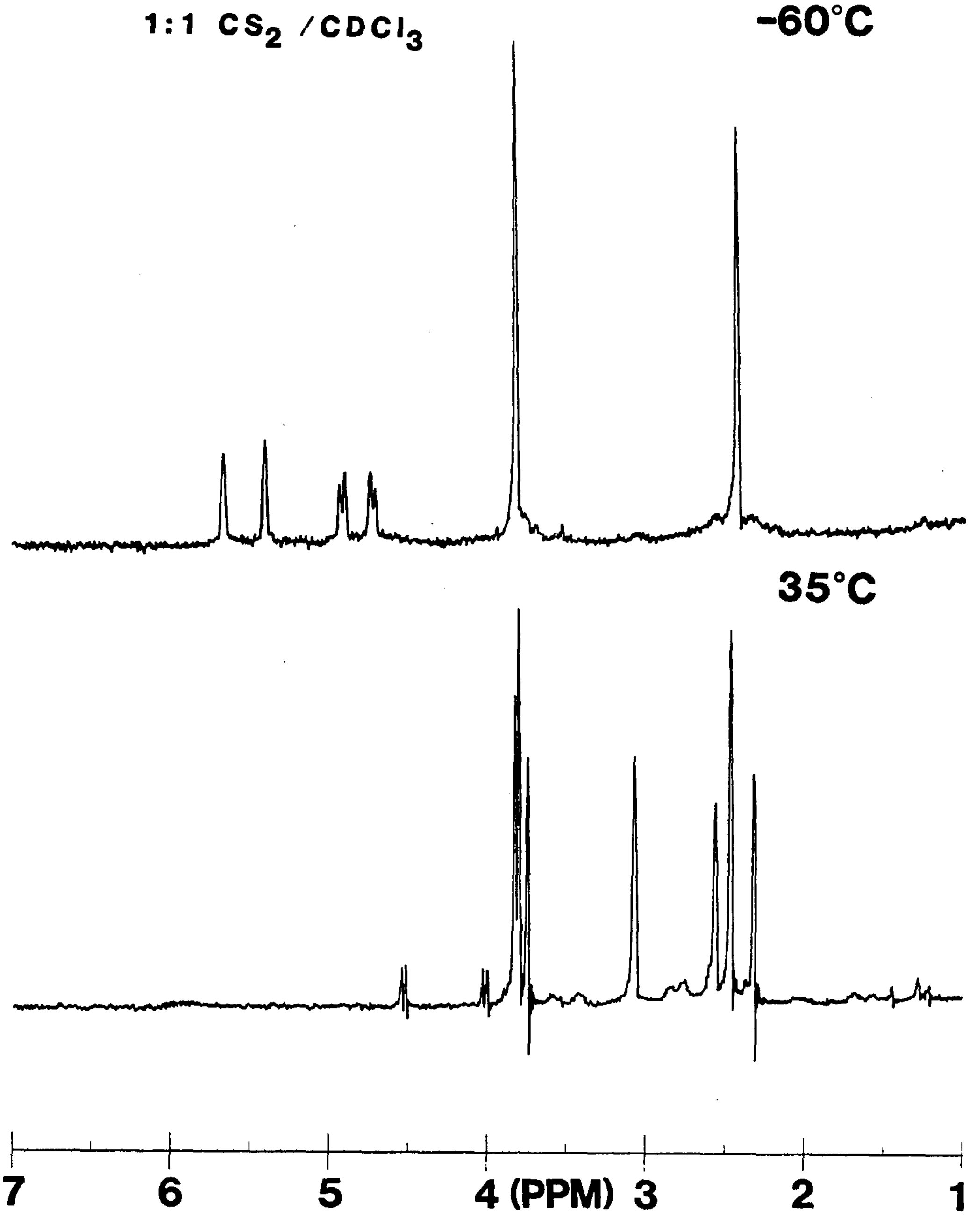


Evidence showing that 27 is the primary pyrolysis product, which later forms 24, 25, and 26, was obtained by recording ^{1}H and ^{13}C NMR spectra of 27 at -60°C. In Figure 1, ^{1}H NMR spectra of the pyrolysis products of 20, recorded at -60 and 35°C, are presented. The ^{1}H NMR spectrum of 27 included one-proton singlets at δ 5.67 and 5.41 for the methylene group at the three position, one-proton doublets (J = 3 Hz) at δ 4.91 and 4.72 for the methylene group at the two position, a three-proton singlet at δ 3.82 for the methyl ester group and a three-proton singlet at δ 2.43 for the ring-methyl group. The ^{13}C NMR spectrum of 27

Figure 1. ^{1}H NMR spectra of the pyrolysis products of 4-carbomethoxy-2,5-dimethyl-3-furylmethyl benzoate (20) recorded at -60°C (top) and at 35°C (bottom)

Top: 2,3-bis(methylene)-4-carbomethoxy-2,3-dihydro-4-methylfuran (27)

Bottom: A mixture consisting of [4+2] dimers 24 and 25 and [4+4] dimer 26. The ratio of the sum of 24 and 25 to [4+4] dimer 26 is 1.24 to 1.


1:1 CS_2 /$CDCl_3$
-60°C
35°C
7
6
5
4 (PPM)
3
2
1

included nine peaks with appropriate chemical shifts including signals at δ 158.03 and 136.20 for ring carbons two and three, respectively, and at δ 103.74 and 85.32 for the exocyclic-methylene carbons at the three and two positions, respectively. The ^{1}H and ^{13}C NMR chemical shifts observed for 27 were assigned by comparing them with the chemical shifts observed for 2,3-bis(methylene)-2,3-dihydrofuran (10),[30] 2,3-bis(methylene)-2,3-dihydro-4-methylfuran,[30] 2,3-bis(methylene)-2,3-dihydro-5-methylfuran and furanoradialene. Warming the samples to room temperature resulted in the dimerization of 27 into 24, 25 and 26.

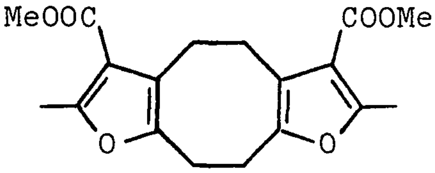
The structures of the [4+2] dimers 24 and 25 were indicated by ^{1}H and ^{13}C NMR spectral data obtained for the product mixtures after [4+4] dimer 26 was removed by selective crystallization. The ^{1}H NMR spectra observed for mixtures of 24 and 25 indicated the presence of only one [4+2] dimer of 27 since the chemical shifts observed for the corresponding hydrogens in 24 and 25 were found to be accidentally equivalent. The ^{1}H NMR spectrum included doublets at δ 4.5 and 3.99 (J = 2.5 Hz) for the exocyclic-methylene hydrogens, broad singlets at δ 3.8 and 3.73 for the carbomethoxy hydrogens, a broad multiplet from δ 2.8 to 2.2 for the ring-methylene hydrogens on the carbons adjacent to the furan ring, broad singlets at δ 2.53 and 2.27

for the ring-methyl groups, and a broad multiplet from δ 1.85 to 1.05 for the remaining ring-methylene hydrogens. The singlets observed at δ 5.67 and 5.41 for the methylene group at the three position in 27 were absent in the ^{1}H NMR spectrum observed for a mixture of 24 and 25. This observation indicated that the exocyclic double bond at the three position acts as the dienophile in forming the observed [4+2] dimers.

The ^{13}C NMR spectrum obtained for a mixture of 24 and 25 indicated that two [4+2] dimers were present in the product mixture. The ^{13}C NMR spectrum included signals at δ 158.79 for the ring carbon attached to an exocyclic methylene group at the two position of a dihydrofuran ring and at δ 85.87 for the corresponding exocyclic methylene carbon. The signals observed in the ^{13}C NMR spectrum of 27 at δ 136.20 for the ring carbon at the three position and δ 103.74 for the exocyclic methylene carbon attached to the three position were absent in the ^{13}C NMR spectrum of the mixture of 24 and 25. This observation provided further evidence that the exocyclic double bond at the three position acts as the dienophile in forming the observed [4+2] dimers. Although the ^{13}C NMR chemical shifts could not be rigorously assigned to regioisomers 24 and 25, the areas of the peaks for the ring-methyl groups were used to determine the isomer ratio of the two [4+2] dimers. The ratio of the sum of the areas of the peaks at δ 14.52 and 14.03 for one isomer to the sum of the areas at δ 15.22 and 14.25 for the other isomer is equal to 2.27 to 1. Although there are six possible [4+2] dimers that can be formed from 27, only [4+2] dimers 24 and 25 were identified in the NMR spectra of the product mixtures. The ^{1}H and ^{13}C NMR chemical shifts observed for [4+2] dimers 24 and 25 were in agreement with the chemical shifts observed for the comparable signals of the [4+2] dimer of furanoradialene.

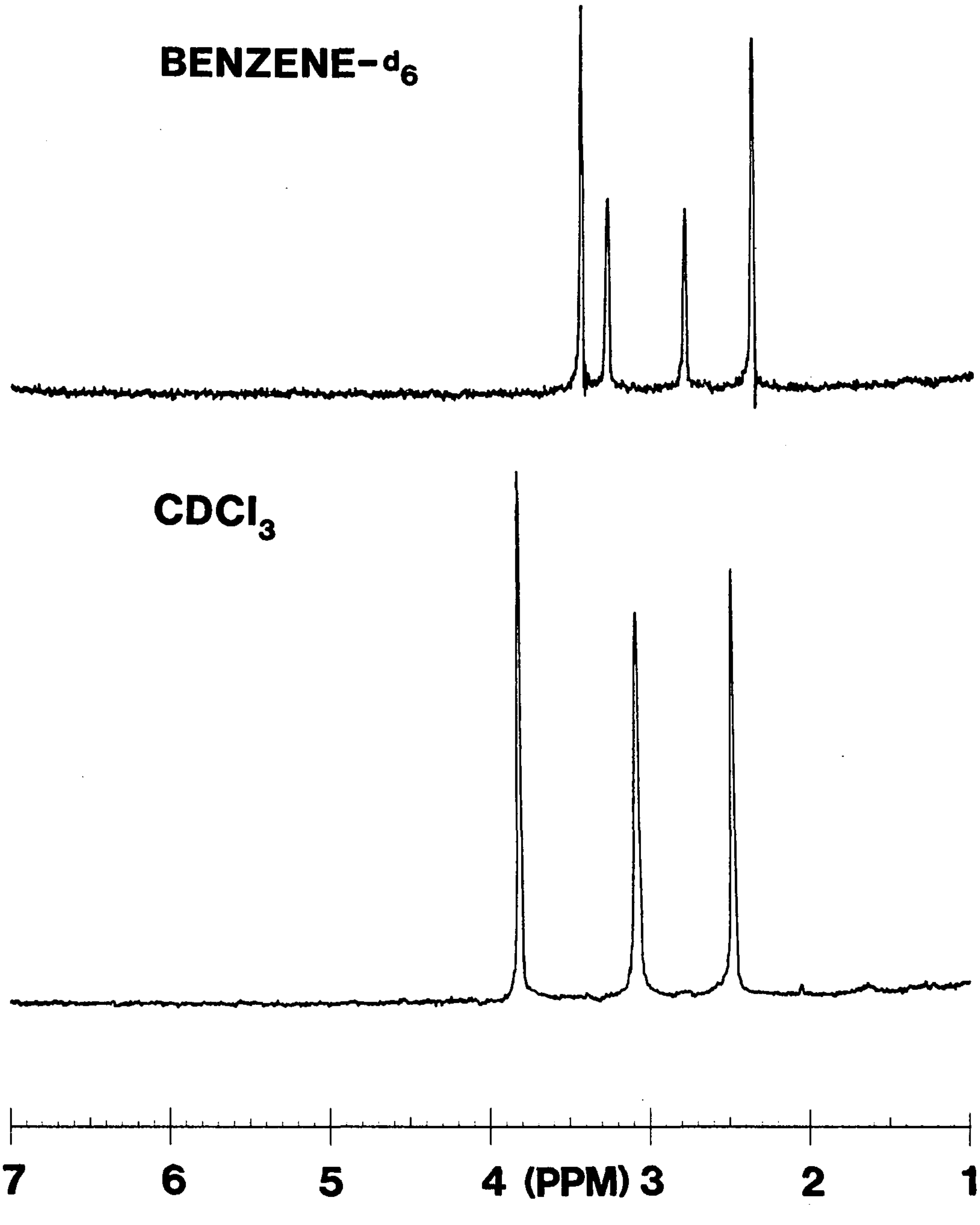
The structure of head-to-head, [4+4] dimer 26 was also indicated by its spectral properties. The ^{1}H NMR spectrum of 26 in benzene-$\underline{d}_6$ included a six-hydrogen singlet at δ 3.43 for the methyl ester groups, four-hydrogen singlets at δ 3.26 and 2.77 for the ring-methylene groups and a six-hydrogen singlet at δ 2.35 for the ring-methyl groups. The ^{1}H NMR chemical shifts of the ring-methylene hydrogens were observed to be accidentally equivalent for a sample of 26 in deuterochloroform. The ^{1}H NMR spectra recorded for benzene-$\underline{d}_6$ and deuterochloroform solutions of 26 are presented in Figure 2. A similar observation was observed in the ^{13}C NMR spectrum of a deuterochloroform solution of 26. The ring-methylene carbons of 26 were found to be

Figure 2. ^{1}H NMR spectra of [4+4] dimer 26, 4,4'-bis-(carbomethoxy)-5,5'-dimethyl-[2,2](2,3)furanophane, recorded in benzene-$\underline{d}_6$ (top) and in deuterochloroform (bottom)



26

Integration of the signals in the top spectrum gave an area ratio of 3:2:2:3, which is the expected ratio for compound 26. Integration of the signals in the bottom spectrum gave an area ratio of 3:4:3 indicating that in deuterochloroform, the signals for the ring-methylene hydrogens are accidentally equivalent.


BENZENE-d_6
$CDCl_3$
7
6
5
4 (PPM) 3
2
1

accidentally equivalent and were observed at δ 29.2. The ^{13}C NMR spectrum of **26** in benzene-d_6 consisted of nine peaks, as required by the symmetry of **26**, with appropriate chemical shifts.

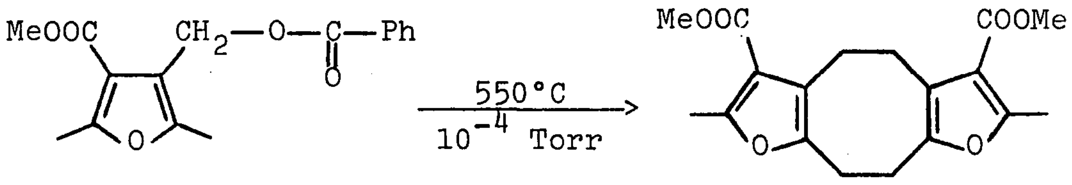
Product yields of dimers **24**, **25**, and **26** were determined by quantitative ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. The yields of products obtained at various pyrolysis temperatures are presented in Table I. Several unsuccessful attempts were made at converting mixtures of **24**, **25**, and **26** into higher amounts of desired [4+4] dimer **26**. Heating a chlorobenzene solution of **24**, **25** and **26** to 100°C in the probe of an NMR spectrometer for 4 h resulted in a gradual decomposition of both the [4+2] dimers **24** and **25** and the [4+4] dimer **26**. There was no evidence obtained which indicated that **24** and **25** could be converted into [4+4] dimer **26**. When the yield of [4+4] dimer **26** from benzoate **20** could not be improved above a maximum of approximately 15%, several alternative syntheses of initial target molecules with general structure **19** were attempted.

Table I. Products and yields formed from pyrolyses of 4-carbomethoxy-2,5-dimethyl-3-furylmethyl benzoate (20) at various temperatures

Pyrolysis Temperature (°C)	Products and Yields (%)[a]		Recovered Starting Material (%)[a]
	[4+2] Dimers	[4+4] Dimer	
	24 + 25	26	20
550[b]	15.2	15.1	3.4
580[b]	17.8	12.6	---
610[b]	15.1	12.2	---

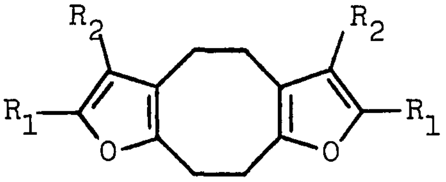
[a] Yields were determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard.

[b] Under all pyrolysis and workup conditions, the major product formed was a colorless, cellophane-like polymer.



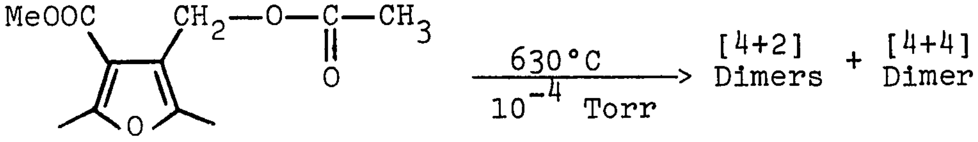
20

26 (15%)



19

Acetate 28 was prepared using a synthetic sequence analogous to that used for the preparation of benzoate 20. Pyrolyses of 28 using a variety of workup conditions gave yields of [4+4] dimer 26 that were lower in all cases than the yields of 26 formed from benzoate 20. The lower product yields from acetate 28 were caused by the partial decomposition of the starting material in the sample compartment and the extensive decomposition of the pyrolysis products because of the presence of acetic acid. The addition of solid sodium bicarbonate in the sample compartment and triethylamine in the liquid-nitrogen-cooled trap to neutralize the acetic acid did not significantly improve the yields of either the [4+2] dimers 24 and 25 or the [4+4] dimer 26.



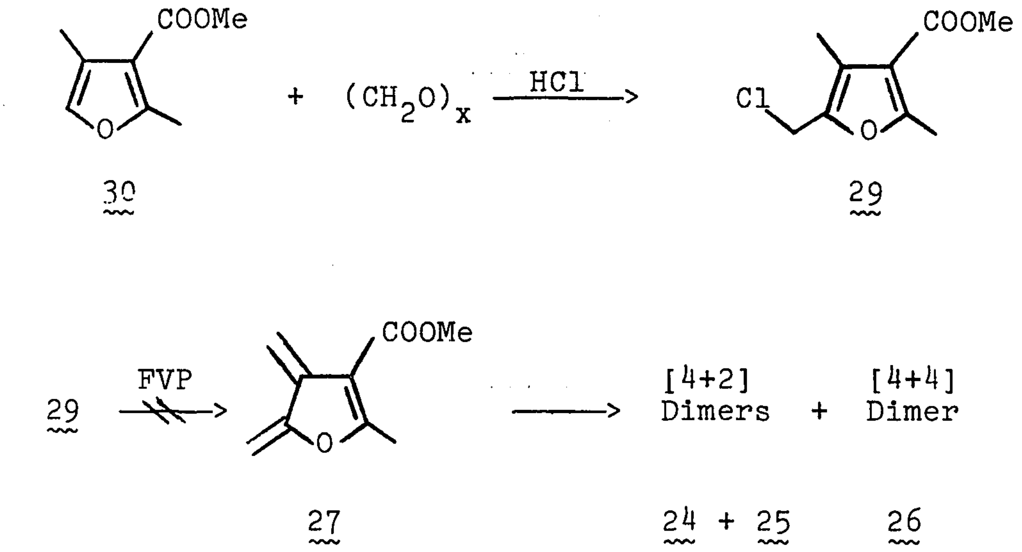
28

24 + 25 26

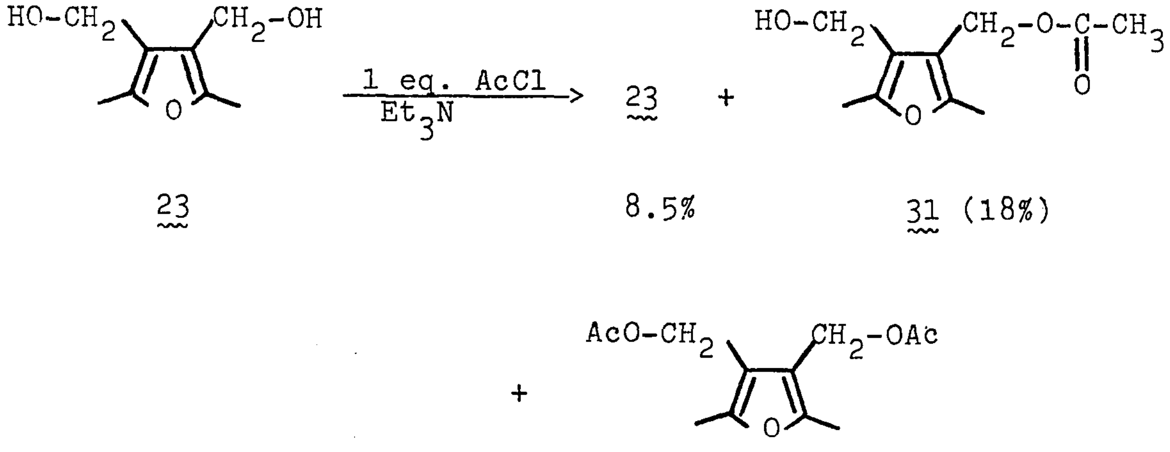
13.5% 8.5%

Since pyrolytic eliminations of hydrogen chloride from *ortho*-methylbenzyl chlorides[15-22] have been used extensively in the preparation of *ortho*-xylylenes, the synthesis and study of the pyrolysis chemistry of 4-carbomethoxy-3,5-dimethylfurfuryl chloride (29) was undertaken. Compound 29 was prepared by chloromethylation of methyl 2,4-dimethylfuran-3-carboxylate (30). Pyrolyses of 29 were carried out at temperatures ranging from 660 to 800°C. At temperatures below 750°C, the only materials collected in the product trap were starting material 29 and polymer. At temperatures above 750°C, the total conversion of 29 into polymeric and decomposed materials was observed. There was no ^{1}H NMR or gas chromatographic (GLC) evidence for the formation of [4+2] dimers 24 and 25 or [4+4] dimer 26 under any pyrolysis or workup conditions. A low-temperature,

^{1}H NMR study of the pyrolysis products failed to give any evidence for the formation of either 2,3-bis(methylene)-4-carbomethoxy-2,3-dihydro-5-methylfuran (27) or any oligomers of 27.



Due to the poor yields and extensive polymerization observed with reactions forming 27 as a precursor to [4+4] dimer 26, syntheses of several alternative [4+4] dimers with general structure 19 were attempted. 2,5-Dimethyl-4-hydroxymethyl-3-furylmethyl acetate (31) was prepared by reacting diol 23 with one equivalent of acetyl chloride in the presence of triethylamine. The desired acetate product 31 was separated from unreacted starting material 23 and diacetate 32 by column chromatography on silica gel. The total yield of isolated product was low because of the partial decomposition of diol 23 and acetate 31 under the chromatography conditions. Pyrolysis of 31 at 590°C resulted in total conversion of the starting material into a complex product mixture. There was no evidence for the formation of desired product 33.

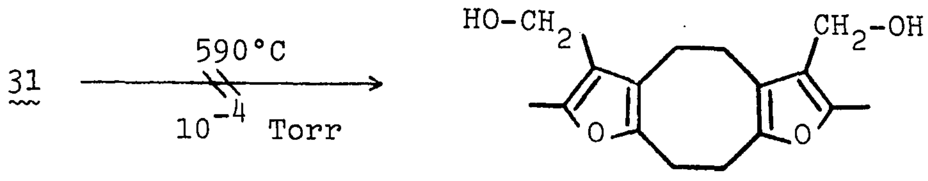


23

8.5%

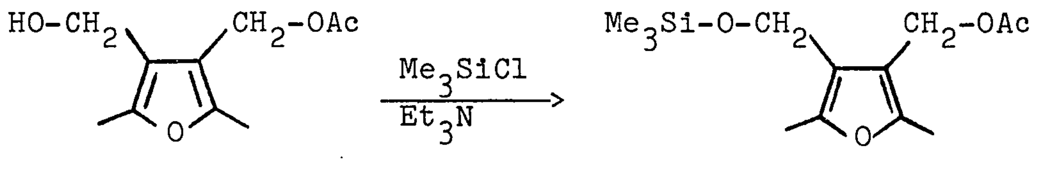
31 (18%)

32 (21.3%)



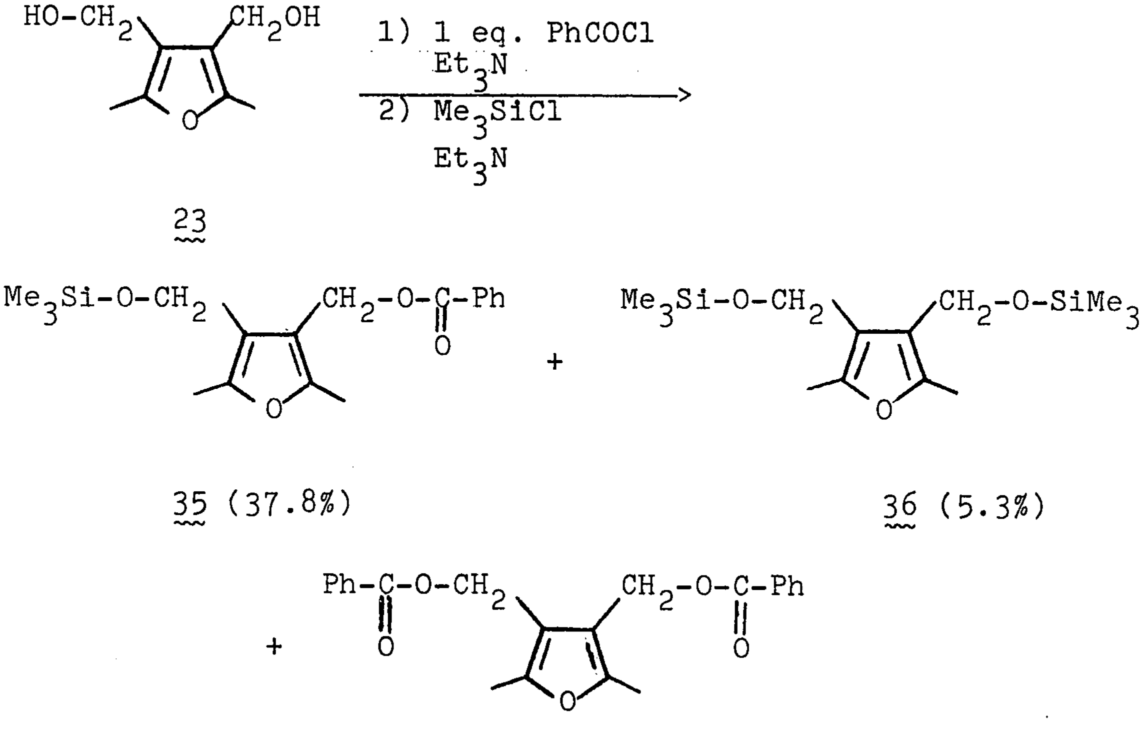
33

Since the hydroxy group in 31 was a possible cause of the lack of formation of 33 from 31, the preparation and pyrolyses of trimethylsilyl ether analogs 34 and 35, of 31, were undertaken. Pyrolyses of either 34 or 35 at



31

34 (90.4%)



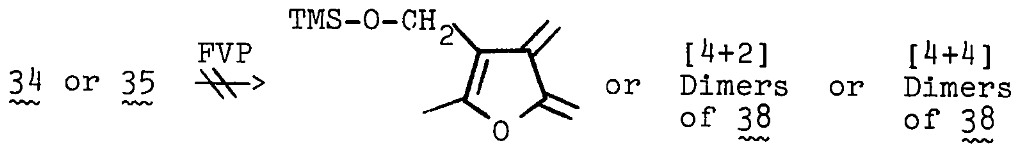
23

35 (37.8%)

36 (5.3%)

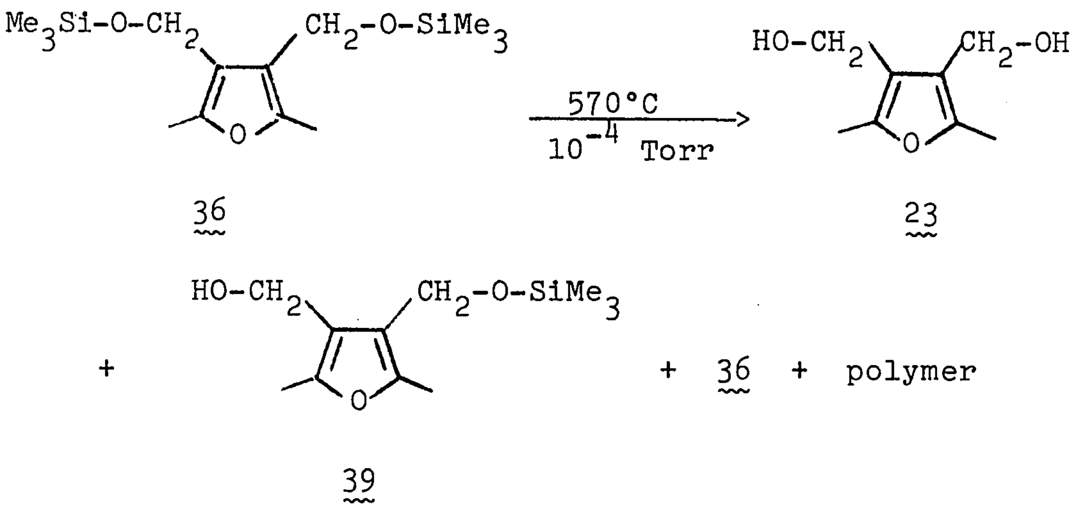
37 (20.5%)

temperatures ranging from 510 to 590°C resulted in total conversion of the starting material into complex product mixtures. There was no ^{1}H NMR evidence for the production of either [4+2] or [4+4] dimers of 2,3-bis(methylene)-2,3-dihydro-5-methyl-4-(trimethylsiloxy)methylfuran (38).



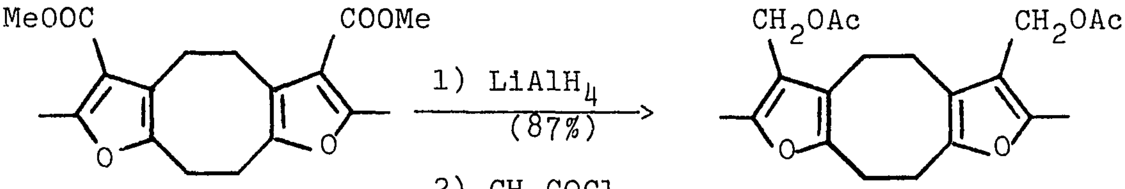
38

Low-temperature, ^{1}H NMR studies of the pyrolysis product mixtures formed from acetate 34 and benzoate 35 also failed to provide conclusive evidence for the production of 38. Since the ^{1}H NMR spectra in the region for the trimethylsilyl groups (δ 0.0 to 0.5) was converted from a singlet in 34 and 35 to multiple peaks in the product mixtures, the trimethylsilyl ether groups in 34 and 35 are apparently unstable to the pyrolysis conditions necessary to form 38. This hypothesis was confirmed by pyrolyzing bis(trimethylsilyl ether) 36. Pyrolysis of 36 at 570°C resulted in the formation of polymer and deprotected alcohols 23 and 39, along with several unidentified biproducts. There was no evidence for the formation of either 38 or oligomers of 38 from pyrolyses of 36.



In the absence of a better method of preparing either [4+4] dimer 26 or an alternative initial target molecule with general structure 19, repetitive pyrolyses of 4-carbomethoxy-2,5-dimethyl-3-furylmethyl benzoate 20 were used to prepare adequate quantities of 26 for an attempted synthesis of $[2_4](2,3,4,5)$furanophane (17). A total of 3.05 g (0.0106 mole) of benzoate 20 was pyrolyzed over nine runs at a furnace temperature of 580°C and pressures ranging from 10^{-4} to 10^{-6} Torr. In each run, the pyrolysis products were dissolved in ca. 30 mL of carbon disulfide at -78°C and then were slowly warmed to room temperature. After removal of the benzoic acid, polymeric byproducts, and carbon disulfide solvent, the desired [4+4] dimer 26 was isolated by selective crystallization from an ether solution of the pyrolysis products. A total of 0.138 g (0.000415 mole; 7.9% of [4+4] dimer 26 was isolated.

[4+4] Dimer 26 was converted in 87% isolated yield into diol 33 by treatment of 26 with an ethereal slurry of lithium aluminum hydride. The resulting diol 33 was then converted into diacetate 40 by treatment of 33 with acetyl chloride in the presence of triethylamine. Using this two-step sequence, 0.105 g of diacetate 40 was isolated. Diacetate 40 was fully characterized by IR, ^{1}H NMR, ^{13}C NMR and high-resolution, mass spectral analyses and gave data which were consistent with its structure. The ^{1}H NMR spectrum of 40, containing five singlets as required by the symmetry of 40, is presented in Figure 3.



2) CH_3COCl, Et_3N (92%)

26

40

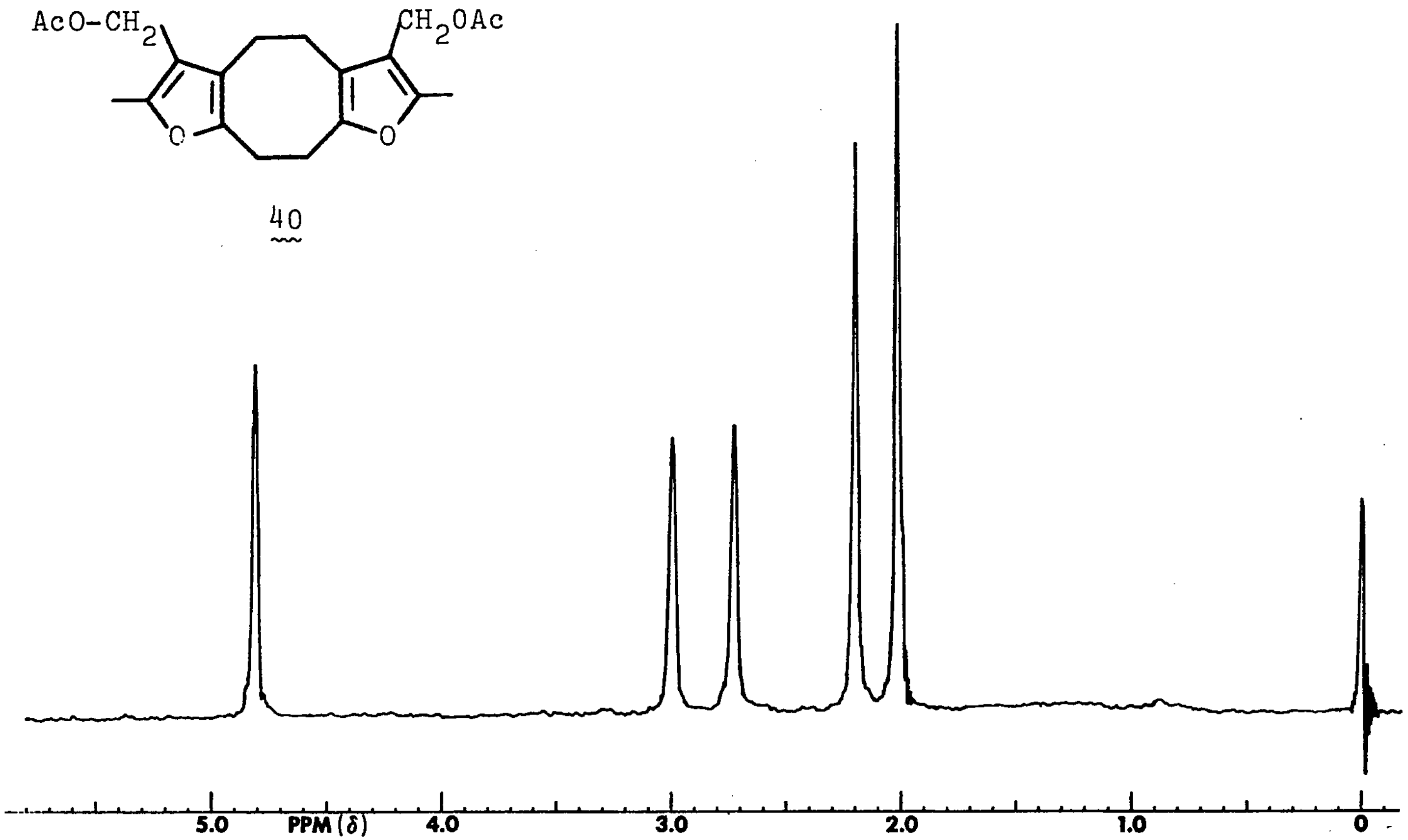
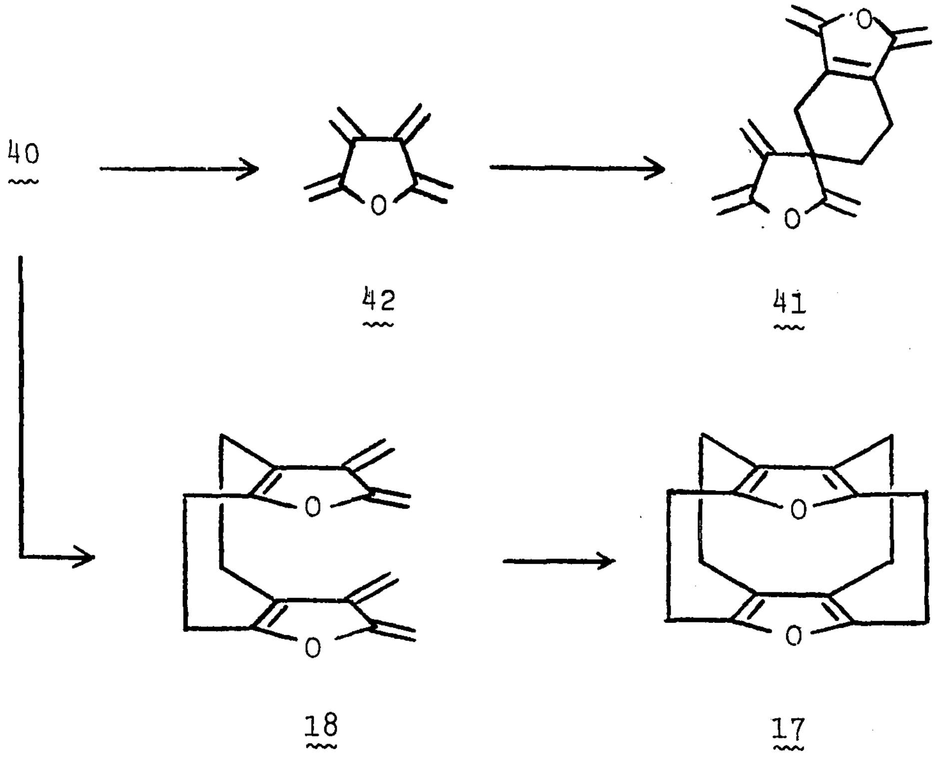


Figure 3. ^{1}H NMR spectrum of a $CDCl_3$ solution of 4,4'-bis(acetoxymethyl)-5,5'-dimethyl-[2,2](2,3)furanophane (40) recorded at ambient temperature

Pyrolyses of diacetate 40 at temperatures ranging from 560 to 610°C resulted in complete conversion of the starting materials into complex product mixtures. ^{1}H NMR spectra of the product mixtures indicated that furanophane 17 and hexaene 18 were at most minor products (<5% yield). The region of the spectra between δ 3.7 and 2.8 for all of the product mixtures included small peaks which might be assigned to the olefinic signals of the [4+2] dimer 41 of furanoradialene 42.



All attempts to isolate $[2_4](2,3,4,5)$furanophane 17 from the product mixtures by thick layer chromatography on silica gel and gas chromatography (GLC) were unsuccessful. Extensive decomposition of the product mixtures occurred on exposure to the separation conditions, resulting in streaking of the product mixtures up the TLC plates with all of the solvent systems tested and more than thirty peaks being observed in the GLC chromatograms.

In order to investigate if furanoradialene 42 is a secondary pyrolysis product formed from hexaene 18, gas chromatography/mass spectral (GLC/MS) analyses of diacetate 40 were obtained at ionization energies of 70 eV and 18 eV. The major fragment ions and their relative percentages are presented in Table II. At the higher ionization energy, the base peak of the fragmentation pattern was observed at m/e 120, corresponding to furanoradialene 42. The fragment at m/e 240, corresponding to $[2_4](2,3,4,5)$furanophane (17) or hexaene intermediate 18, was 14% of the base peak at 70 eV. These observations differ from those observed at 18 eV, in which the base peak of the fragmentation pattern at m/e 240 corresponds with furanophane 17 or hexaene 18. At the lower ionization energy, the major fragment ions are formed by losses of either one or two molecules of

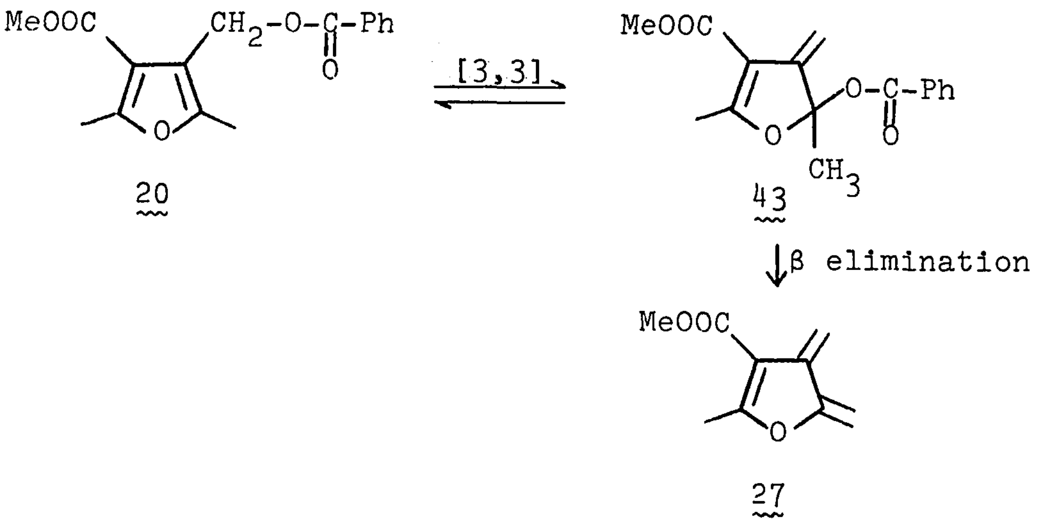
Table II. Gas chromatography/mass spectral analyses of 4,4'-bis(acetoxymethyl)-5,5'-dimethyl-[2.2](2,3)-furanophane (40) at ionization energies of 70 eV and 18 eV

	70 eV	18 eV	
Mass Number (m/e)	% of Base Peak	% of Base Peak	Fragment Ion
360	2.78	71.94	M^+
300	3.42	58.72	$(M^+) - CH_3COOH$
240	14.00	100.00	$(M^+) - 2(CH_3COOH)$
180	9.93	4.72	$(M^+)/2$
120	100.00	13.10	$[(M^+) - 2(CH_3COOH)]/2$

acetic acid from 40. At the higher ionization energy, the major fragment ion is due to cleavage into two furanoradialene fragments 42, after the loss of two molecules of acetic acid from 40. These observations suggest that the loss of two molecules of acetic acid from 40 to form either furanophane 17 or hexaene 18, occurs more readily than the cleavage which results in the formation of furanoradialene 42.

DISCUSSION

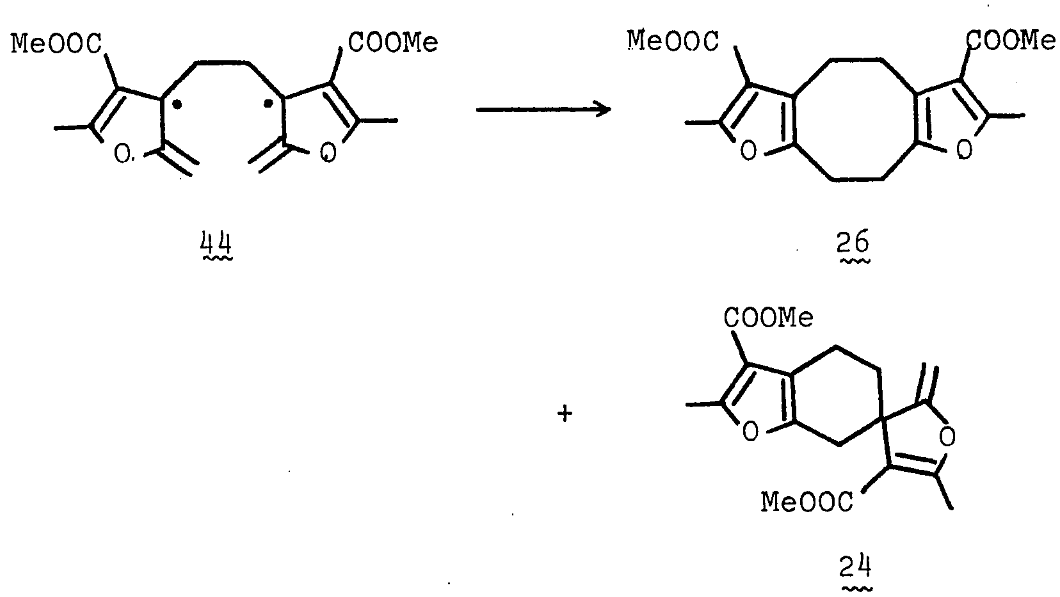
A migration mechanism was previously proposed for the conversion of 2-methyl-3-furylmethyl benzoate (9) into 2,3-dimethylene-2,3-dihydrofuran (10).[30] A similar mechanistic scheme is proposed for the conversion of 4-carbomethoxy-2,5-dimethyl-3-furylmethyl benzoate (20) into 2,3-bis(methylene)-4-carbomethoxy-2,3-dihydro-5-methylfuran (27). The mechanism involves a β elimination of benzoic acid from intermediate 43 after a [3,3] shift of the benzoate group. This formal 1,4 elimination of a carboxylic acid during an ester pyrolysis has literature precedent in the pyrolysis chemistry of allylic[48-53] and benzylic[54-56] esters containing δ hydrogens. In the

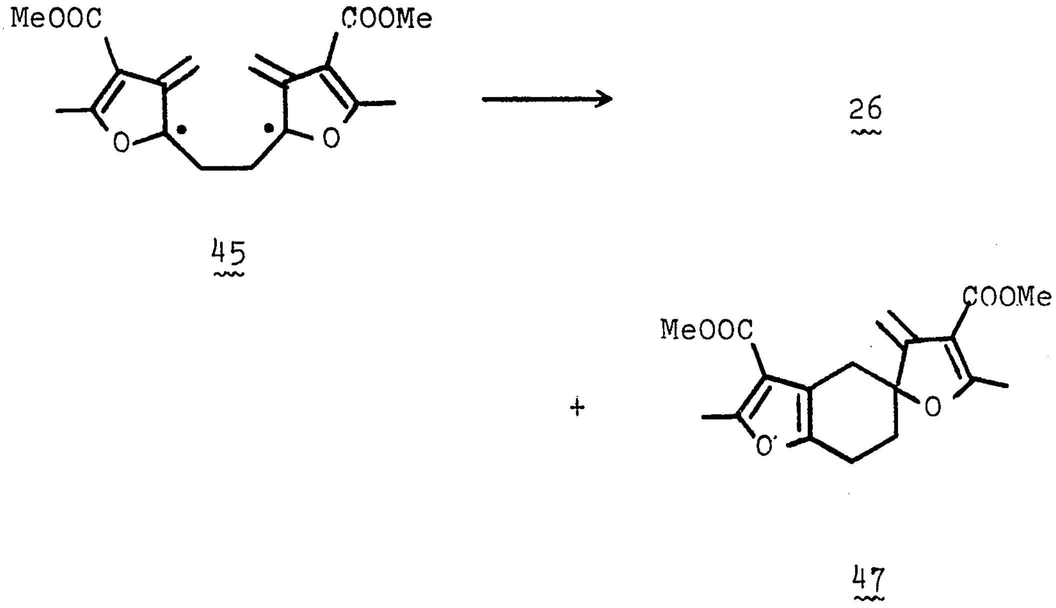


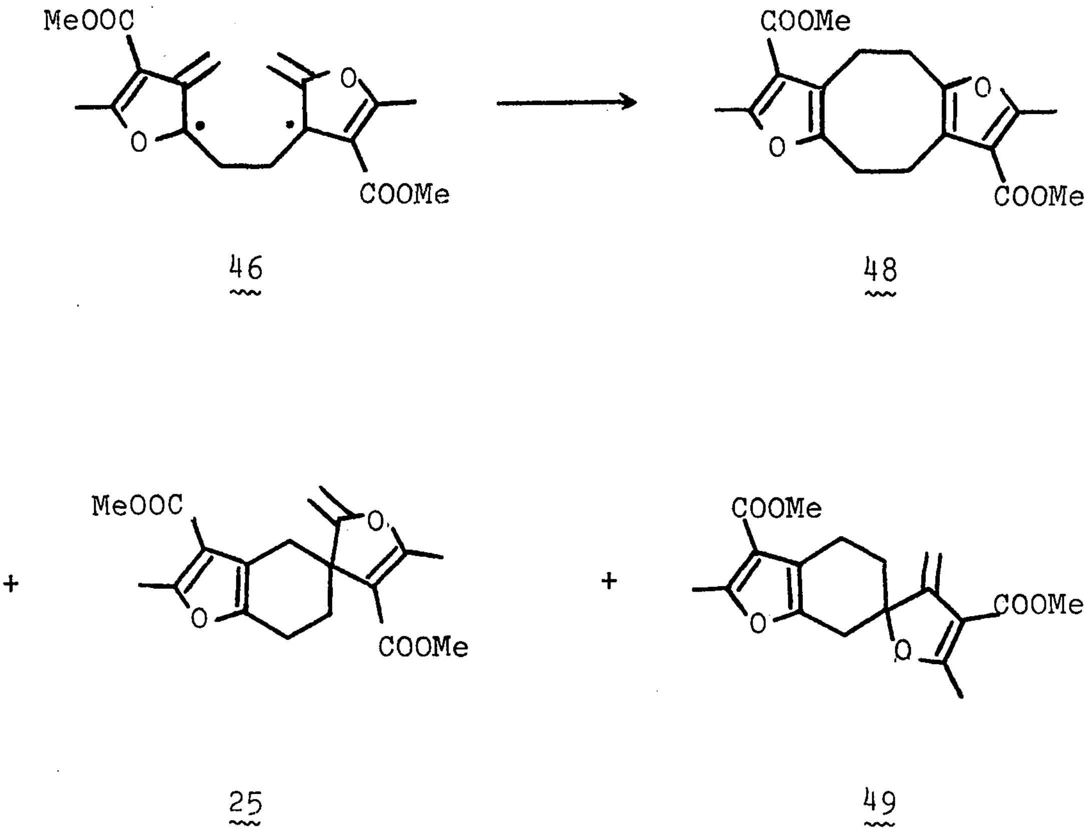
product mixtures formed from several allylic esters, the intermediates formed by a [3,3] shift of a carboxylate group have been isolated.[51,52,57-63]

The dimerization of **27** forming [4+2] dimers **24** and **25** and [4+4] dimer **26** can involve either concerted or diradical mechanisms or a combination of both. There are three possible diradical intermediates which can be formed from **27**: **44**, **45**, and **46**. Diradical **44** can form one of the observed [4+2] dimers **24** in addition to the observed [4+4] dimer **26**. Diradical **45** can form both the observed [4+4] dimer **26** and an unobserved [4+2] dimer **47**. Diradical **46** can form the unobserved head-to-tail, [4+4] dimer **48** and the unobserved [4+2] dimer **49**, as well as the observed [4+2] dimer **25**.

Simple resonance considerations suggest that the type of radical center found in **44** is more stable than that found in **45**. However, if there is a stability difference in the type of radical centers found in **44** and **45**, one of the symmetrical, diradical intermediates (**44** or **45**) would be more stable than either the other symmetrical, diradical intermediate or the unsymmetrical, diradical intermediate **46**. The diradical mechanism for the formation of [4+4] dimer **26** is analogous to that proposed for the dimerization of *ortho*-xylylene (**8**),[64] trimethylenecyclobutane,[65] and tetramethylenecyclobutane.[66]


MeOOC
COOMe
O
O
44
MeOOC
COOMe
O
O
26
+
COOMe
O
O
MeOOC
24

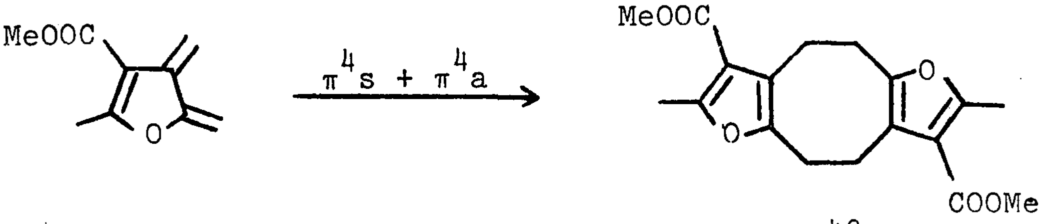

MeOOC
COOMe
O
O
45
26
+
MeOOC
COOMe
O
O
47



46 48

25 49

A concerted ($\pi^4s + \pi^4a$) mechanism for the dimerization of 27 could result in the formation of either the observed, head-to-head, [4+4] dimer 26 or the unobserved, head-to-tail dimer 48. The information obtained from a molecular orbital calculation on structure 27 would be necessary to predict which [4+4] dimer (48 or 26) would be formed from a concerted dimerization of 27.

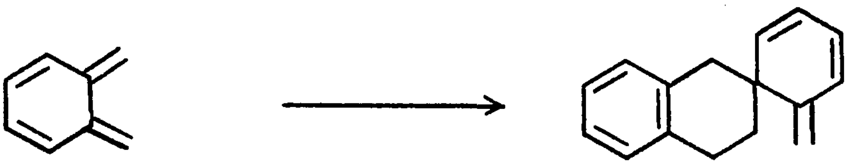


27

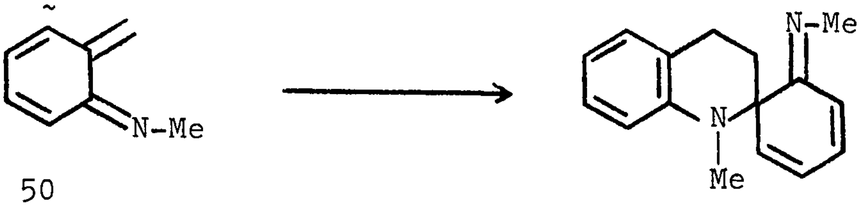
48

or 26

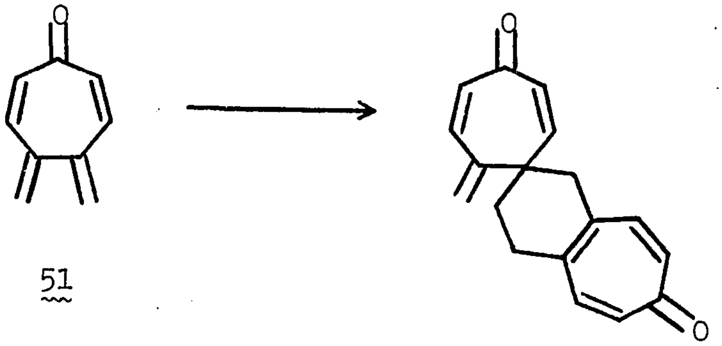
A concerted mechanism is favored for the formation of the [4+2] dimers from 27 since diradical intermediates 44, 45 and 46 would be expected to produce some of the unobserved [4+2] dimers 47 and 49 in addition to the observed dimers 24 and 25. However, the possibility that some of the total amount of [4+2] dimers 24 and 25 may result from a diradical pathway can not be ruled out. The formation of [4+2] dimers 24 and 25 has literature precedent in the formation of spirodimers from *ortho*-xylylene (8),[64] imine 50[67] and 4,5-bis(methylene)cyclohepta-2,6-dien-1-one (51).[68]



8



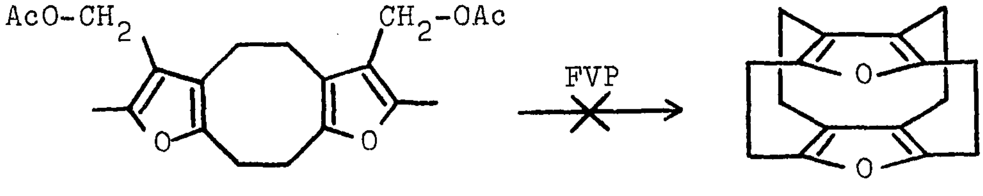
50



51

The poor yields of the desired [4+4] dimer 26 from triene 27 can be attributed to several factors. The uncontrolled polymerization of 27 resulted in the formation of a colorless, transparent polymer as the major product under all pyrolysis and workup conditions. Also, for the first time, formation of [4+2] dimers predominated over formation of [4+4] dimers on warmup of a 2,3-bis(methylene)-2,3-dihydrofuran species. Although the extensive polymerization observed in this system might explain the poor yields of [4+4] dimer 26, the 17.8% yield of [4+2] dimers 24 and 25, formed on pyrolysis of benzoate 20 at 580°C, is the highest yield of [4+2] dimers formed to date from a 2,3-bis(methylene)-2,3-dihydrofuran species. The extent of the formation of the [4+2] dimers from 27 is unusual and at this time we do not have a satisfactory explanation for this observation.

The investigation of the pyrolysis chemistry of 4,4'-bis(acetoxymethyl)-5,5'-dimethyl-[2.2](2,3)furanophane (**40**) showed that **40** was at best a poor precursor to $[2_4]$(2,3,4,5)furanophane (**17**). A mechanistic scheme which

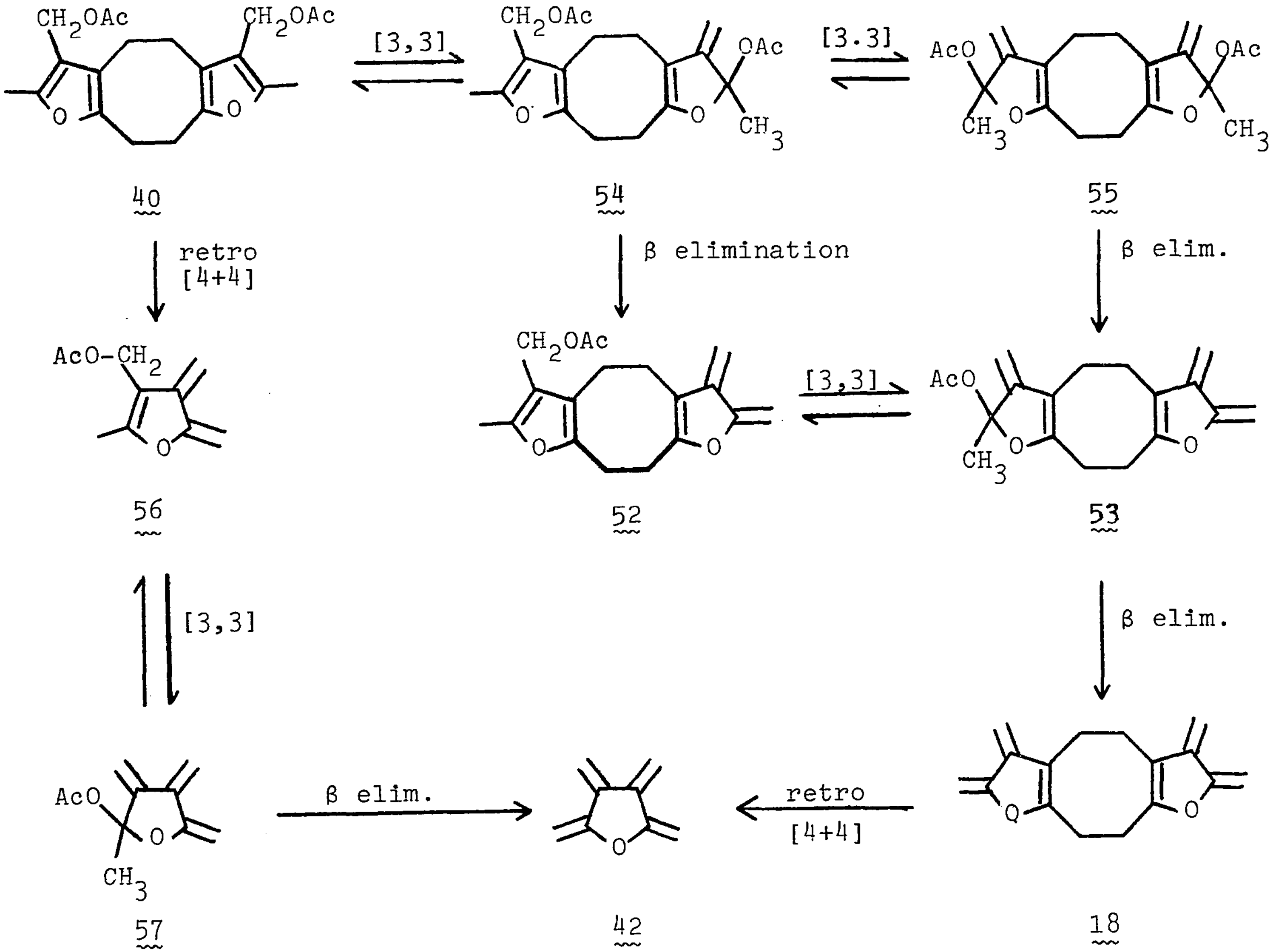


40 **17**

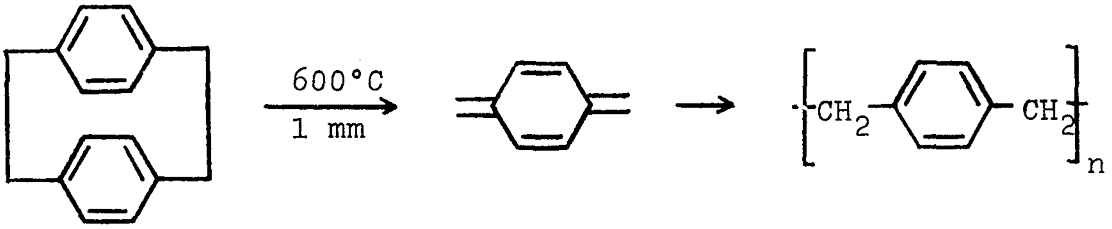
accounts for the formation of the pyrolysis products from **40** is presented in Figure 4. The desired hexaene intermediate **18** can be formed from diacetate **40** by undergoing two β eliminations of acetic acid after [3,3] shifts of the acetate groups into the furan rings.

The formation of [4+2] dimer **41** of furanoradialene (**42**) can be explained by retro [4+4] reactions of either hexaene intermediate **18** or structures **52** and **53** to form furanoradialene (**42**). Structures **52** - **55** and **40** would also be expected to form **56** or **57** which would be converted to **42** under the pyrolysis conditions. Furanoradialene (**42**) then undergoes a Diels-Alder dimerization upon workup, forming [4+2] dimer **41**. The retro [4+4] reaction observed in the pyrolysis of diacetate **40** is analogous to the retro [6+6] reaction observed in [2.2](1,4)cyclophane systems. A commercial process developed by Union Carbide

Figure 4. Mechanistic scheme for the formation of furanoradialene (**42**) and 4,4',5,5'-tetrakis(methylene)4,4',5,5'-tetrahydro[2.2](2,3)furanophane (**18**) from 4,4'-bis(acetoxymethyl)-5,5'-dimethyl-[2.2](2,3)-furanophane (**40**)

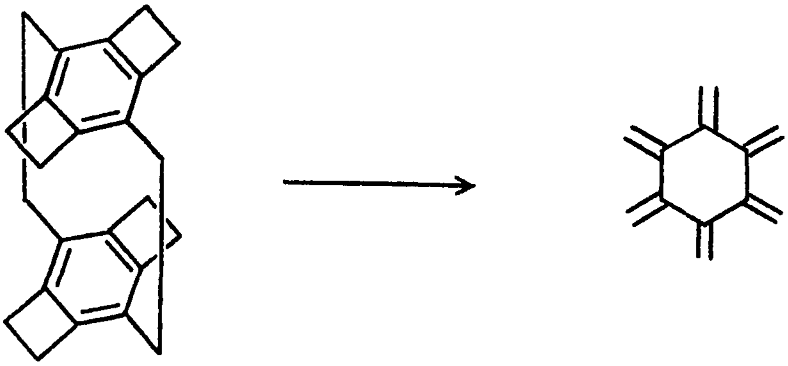

CH2OAc
CH2OAc
40
[3,3]
54
[3.3]
55
retro
[4+4]
β elimination
β elim.
56
52
[3,3]
53
[3,3]
β elim.
57
β elim.
42
retro
[4+4]
18

for the production of Parylene (**58**), a family of linear plastics based on the polymerization of p-xylylene (**59**), involves the generation of **59** by a gas-phase pyrolysis of [2.2](1,4)cyclophane (**1**) at 600 - 650°C.[69,70] When deposited onto a substrate, p-xylylene (**59**) instantly polymerizes in a continuous film. A similar situation



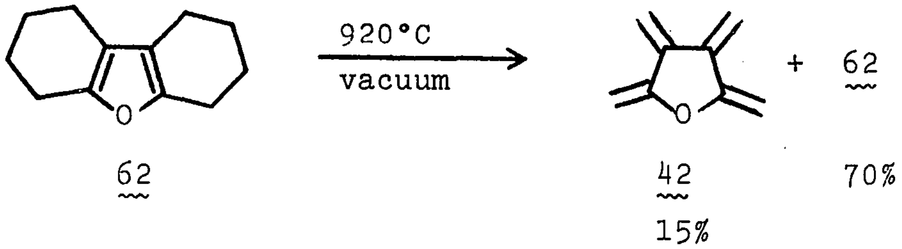
1 **59** **58**

resulted when cyclophane **60** was pyrolyzed at 900°C in the gas phase, producing hexaradialene (**61**).[71] A



60 **61**

related reaction involves the production of furanoradialene (**42**) from pyrolyses of 1,2,3,4,6,7,8,9-octahydrodibenzofuran (**62**).[72]



The retro [4+4] reaction observed during pyrolyses of diacetate 40 rendered 40 a poor precursor to $[2_4]$-(2,3,4,5)furanophane (17). The temperatures required for generating 2,3-bis(methylene)-2,3-dihydrofuran species from 40 are high enough for the undesirable retro [4+4] reaction to occur.

EXPERIMENTAL

Methods and Materials. The pyrolysis apparatus has been previously described.[73] ^{1}H NMR spectra were recorded using Varian EM-360, Varian HA-100, Hitachi-Perkin Elmer R-20B or Bruker WM-300 spectrometers. ^{13}C NMR spectra were recorded using a JEOL FX-90Q or a Bruker WM-300 spectrometer. Chemical shifts are reported in parts per million (δ) from tetramethylsilane (Me_4Si). Infrared spectra were measured with a Beckman 4250 spectrophotometer. High resolution mass spectra were measured with an Associated Electronics Industries MS-902 instrument at 70 eV. Gas Chromatography/mass spectral analyses (GLC/MS) were performed using a Finnigan 4000 instrument, at ionization energies of 10 to 70 eV, with an INCOS 2300 data system. GLC analyses were performed using a Hewlett Packard 5840A instrument equipped with a 25 meter, fused-silica, capillary column coated with a methylsilicone liquid phase. Melting points were determined with a Thomas-Hoover apparatus and are uncorrected.

Chloroacetone and chlorotrimethylsilane were obtained from Aldrich Chemical Co. Lithium aluminum hydride (lithium tetrahydridoaluminate) was obtained from Alfa Products. A 50% dispersion of sodium hydride in mineral oil was obtained from J. T. Baker Chemicals. Acetyl chloride, benzoyl chloride, methyl acetoacetate and triethylamine were supplied by Eastman Organic Chemicals. Iodine and paraformaldehyde were obtained from Fisher Scientific Co. Gaseous hydrogen chloride was obtained from Matheson Co.

Dimethyl 2,3-Diacetylsuccinate. The following procedure was adapted from a literature synthesis of diethyl 2,3-diacetylsuccinate.[74,75] To a mechanically stirred slurry of 12.46 g (0.519 mole) of sodium hydride (24.92 g of a 50% dispersion in mineral oil which was washed four times with 150 mL of Skelley B) in 1 L of dry ether ($LiAlH_4$) at 0°C, was slowly added a solution of 58.06 g (0.5 mole) of freshly distilled methyl acetoacetate in 50 mL of dry ether (dropwise addition over a 1 h period). Ether was added when necessary to facilitate stirring (ca. 300 mL total). The reaction mixture, consisting of a white solid suspended in ether, was stirred at 0°C for 1 h. A suspension of 65.87 g (0.26 mole) of iodine in a total of ca. 500 mL ether was added slowly over a 1.5 h period. The mixture was then stirred vigorously as the temperature was allowed to equilibrate from 5°C to room temperature over a 10 h period. After the addition of 250 mL of distilled water, the mixture was stirred for 1 h. The ether layer was concentrated to a volume of ca. 100 mL by heating the open reaction flask. The white solids suspended between the ether and aqueous layers were collected by suction filtration, yielding 26.67 g (0.1158 mole; 46.34%) of a mixture of meso- and d,l-dimethyl 2,3-diacetylsuccinate: mp 138-139°C; IR ($CHCl_3$) 1745, 1720, 1645, 1290-1245, 1165 cm^{-1}; ^1H NMR ($CDCl_3$) (major isomer) δ 4.52 (s, 2H), 3.72 (s, 6H), 2.44 (s, 6H); ^1H NMR ($CDCl_3$) (minor isomer) δ 4.48 (s, 2H), 3.75 (s, 6H), 2.38 (s, 6H); high resolution mass spectrum calcd for $C_{10}H_{14}O_6$ 230.07904, measured 230.07863. The ether and aqueous filtrates were separated and the aqueous layer was extracted with ethyl acetate (4 x 50 mL). The ether and ethyl acetate layers were combined and then washed with saturated sodium chloride (3 x 50 mL), dried over $MgSO_4$ and concentrated, yielding an additional 4.73 g (0.021 mole; 8.2%) quantity of dimethyl 2,3-diacetylsuccinate.

Dimethyl 2,5-dimethyl-3,4-furandicarboxylate (21). An adaptation of a literature synthesis of diethyl 2,5-dimethyl-3,4-furandicarboxylate was used.[75,76] Dimethyl 2,3-diacetylsuccinate (26.67 g; 0.116 mole) was dissolved in 200 mL of cold, concentrated sulfuric acid. After stirring the mixture for 4 h at 0°C, it was poured over cracked ice in a 1 L beaker. After the ice had melted, 200 mL of ether was added and the layers were separated. The aqueous layer was extracted with ether (6 x 100 mL). The ether layers were combined and then washed with saturated sodium bicarbonate (4 x 100 mL) and saturated sodium chloride (3 x 100 mL). After the organic layer was dried ($MgSO_4$), the solvent was removed giving the crude product (23.07; 0.109 mole; 94%) which was purified by recrystallization from Skelly B, yielding 18.22 g (0.086 mole; 74%) of colorless, platelike crystals of 21: mp 63.5-64°C; IR ($CHCl_3$) 2970, 1715, 1600, 1455, 1415, 1290, 1095, 865 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.83 (s, 6H), 2.43 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 164.0, 155.8, 113.6, 51.6, 13.1; high resolution mass spectrum calcd for $C_{10}H_{12}O_5$ 212.06848, measured 212.06830.

4-Carbomethoxy-2,5-dimethyl-3-furylmethyl Benzoate (20). To a stirred solution of 16.39 g (0.077 mole) of dimethyl 2,5-dimethyl-3,4-furandicarboxylate (21) in 300 mL of dry ether ($LiAlH_4$), was slowly added 1.6180 g (0.0426 mole) of lithium aluminum hydride powder. After the addition was completed, the mixture was stirred at room temperature for 4 h. A standard workup[77] yielded 13.12 g of a mixture containing starting material 21, 4-carbomethoxy-2,5-dimethyl-3-furylmethyl alcohol (22) and 3,4-bis(hydroxymethyl)-2,5-dimethylfuran (23). Without purification, the hydroxy groups present in compounds 22 and 23 were converted to their benzoate derivatives. A solution of 12.9832 g (0.0924 mole) of benzoyl chloride in 40 mL of dry ether was added dropwise to a stirred solution containing 13.12 g of the mixture of compounds 21, 22 and 23 and 13.1029 g (0.1295 mole) of triethylamine in 150 mL of dry ether. After the mixture was stirred for 24 h at room temperature, 50 mL of distilled water was added and the layers were separated. The aqueous layer was extracted with ether (3 x 25 mL). The ether layers were combined and then washed with water (3 x 50 mL), 1 M hydrochloric acid (3 x 50 mL), saturated sodium bicarbonate (3 x 50 mL) and saturated sodium chloride (2 x 50 mL). After the organic layer was dried ($MgSO_4$), the solvent was removed giving 23.33 g of crude product. The product mixture was purified initially by selective crystallization from a concentrated ether solution, yielding 4.5636 g (0.0125 mole; 16.22%) of clear prisms of 3,4-bis(benzoyloxymethyl)-2,5-dimethylfuran (37): mp 97-98°C; IR ($CHCl_3$) 3100-2790, 1720, 1622, 1265, 1170, 1100, 1020, 915, 856, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.14-7.80 (m, 4H), 7.65-7.03 (m, 6H), 5.24 (s, 4H), 2.33 (s, 6H); high resolution mass spectrum calculated for $C_{22}H_{20}O_5$ 364.13108, measured 364.13145. The remainder of the product mixture was separated by column chromatography on 180 g of silica gel (Baker 40-140 mesh) using a 2:3 mixture of methylene chloride in hexanes as the eluant. The material eluting first from the column was a small amount of impure dibenzoate 37. The second material eluting from the column was 3.5851 g (0.0124 mole; 16.11%) of 4-carbomethoxy-2,5-dimethyl-3-furylmethyl benzoate (20): IR (thin film) 3110-2800, 1715, 1705, 1585, 1445, 1295, 1265, 1205, 1130, 1095, 1075 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.35-8.0 (m, 2H), 7.75-7.25 (m, 3H), 5.46 (s, 2H), 3.85 (s, 3H), 2.58 (s, 3H), 2.38 (s, 3H); high resolution mass spectrum calcd for $C_{16}H_{16}O_5$ 288.09978, measured 288.09937. The material eluting last from the column was 4.8213 g (0.02272 mole; 29.43%) of starting material 21.

General Pyrolysis Procedure. The pyrolyses were run at temperatures from 550 to 750°C. A sample of the furylmethyl ester in a Pyrex boat was placed into the sample compartment and the compartment was heated to temperatures between 50 and 150°C. A condenser cooled to ca. -20°C was placed between the furnace and the liquid-nitrogen-cooled trap to collect any unreacted starting material and benzoic acid formed as a byproduct in pyrolyses of benzoates 20 and 35. During each pyrolysis, a solvent was transferred from a flask into the product trap. After all of the starting material had distilled out of the sample compartment, nitrogen was introduced into the system and an internal standard was added to the trap. The product mixture was then warmed to -78°C and solvent at -78°C was used to rinse any product remaining on the insert of the trap to the bottom. The product solution was mixed by using it to rinse the walls of the trap several times. For the low-temperature, ^{1}H NMR experiments, the product solution was placed into NMR tubes at -78°C and NMR spectra were recorded at temperatures below -60°C. After the tubes were warmed to 0°C, NMR spectra were again recorded. For preparative runs, the product solution at -78°C was slowly warmed to room temperature. The solution was then washed with 1 M sodium bicarbonate, dried over magnesium sulfate and concentrated, yielding the product residue.

Pyrolysis of 4-Carbomethoxy-2,5-dimethyl-3-furylmethyl Benzoate (20) (Yield Maximization). Samples of benzoate 20 (ca. 0.22 g) were pyrolyzed at temperatures of 550, 580 and and 610°C and pressures of ca. 10^{-4} Torr using the general procedure. During a pyrolysis, 10 mL of carbon disulfide at -78°C was deposited into the trap. After the apparatus was shut down under nitrogen, the trap was warmed to -78°C and 10 mL of carbon disulfide was used to rinse any material on the insert of the trap to the bottom. After 30 min at -78°C, the trap was warmed to 0°C and maintained at that temperature for 12 h. The product mixture was then warmed to room temperature. After removal of the carbon disulfide solvent, the product residue was dissolved in ether and washed with water (2 x 10 mL), 1 M sodium bicarbonate (3 x 10 mL) and saturated sodium chloride (2 x 10 mL). After the organic layer was dried ($MgSO_4$), the solvent was removed giving the crude product mixture which was dissolved in a $CDCl_3$ solution containing a known amount of 1,1,2,2,-tetrachloroethane as an internal standard. Yields were determined by quantitative, ^1H NMR experiments and are presented in Table I.

Preparative Scale Pyrolyses of 4-Carbomethoxy-2,5-dimethyl-3-furylmethyl Benzoate (20). A total of 3.05 g (0.0106 mole) of benzoate 20 was pyrolyzed using the general procedure over nine runs at a furnace temperature of 580°C and pressures ranging from 10^{-4} to 10^{-6} Torr. During a pyrolysis, 15 mL of carbon disulfide was distilled from a flask into the product trap. After the apparatus was shut down under nitrogen, the trap was warmed to -78°C and 15 mL of carbon disulfide at -78°C was used to rinse the materials on the walls of the trap to the bottom. After 15 min at -78°C, the product solution was warmed to 0°C and maintained at that temperature for 13 h. The solution was warmed to room temperature and after the solvent was removed, the residue was dissolved in ether and washed with water (2 x 10 mL), saturated sodium bicarbonate (3 x 10 mL) and saturated sodium chloride (2 x 10 mL). After the solution was dried ($MgSO_4$), the solvent was removed yielding the crude product mixture. The crude product mixtures from nine runs were combined and purified by selective crystallization from ether, yielding 0.138 g (0.000415 mole; 7.9%) of white needles of 4,4'-bis(carbomethoxy)-5,5'-dimethyl-[2.2](2,3)furanophane (26): mp 180-181.5°C, ^{1}H NMR ($\underline{d}_6$-benzene) δ 3.43 (s, 6H), 3.26 (s, 4H), 2.77 (s, 4H), 2.35 (s, 6H); ^{1}H NMR ($CDCl_3$) δ 3.82 (s, 6H), 3.08 (broad s, 8H), 2.48 (s, 6H); ^{13}C NMR ($\underline{d}_6$-benzene) δ 164.64, 157.43, 148.49, 119.45, 114.47, 50.38, 25.79, 23.35, 14.19; ^{13}C NMR ($CDCl_3$) δ 164.96, 157.97, 150.17, 118.32, 112.63, 50.86, 29.20, 14.19; high resolution mass spectrum calcd for $C_{18}H_{20}O_6$ 332.12599, measured 332.12654. After removing most of furanophane (26), the product mixture consisted mainly of [4+2] dimers 24 and 25: ^{1}H NMR (1:1 CS_2/$CDCl_3$) δ 4.5 (d, J = 2.5 Hz, 2H), 3.99 (d, J = 2.5 Hz, 2H), 3.8 (s, 6H), 3.73 (s, 6H), 2.8-2.2 (broad m, 8H), 2.53 (s, 6H), 2.27 (s, 6H), 1.85-1.05 (broad m, 4H); ^{13}C NMR ($CDCl_3$) δ 166.69, 165.83, 165.23, 164.85, 158.79, 148.28, 147.03, 116.75, 116.58, 112.47, 110.95, 85.87, 50.92, 50.76, 47.94, 32.23, 30.28, 17.44, 15.22, 14.52, 14.25, 14.03. The ratio of one [4+2] dimer to the other is estimated to be 2.27 : 1 based on the ratio of the areas for the ring methyl groups present in each regioisomer.

2,3-Bis(methylene)-4-carbomethoxy-2,3-dihydro-5-methylfuran (27). A 0.3998 g (0.001387 mole) quantity of 20 was pyrolyzed at 610°C and 10^{-5} Torr using the general procedure. The pyrolysis products were dissolved in a total of 4 mL of a 1 : 1 mixture of carbon disulfide and deuterochloroform. After the product solution was placed into three 5 mm, NMR tubes containing Me_4Si at -78°C, ^1H and ^{13}C NMR spectra were recorded at temperatures below -60°C which indicated the presence of 2,3-bis(methylene)-4-carbomethoxy-2,3-dihydro-5-methylfuran (27): ^1H NMR (1:1 $CS_2/CDCl_3$) δ 5.67 (s, 1H), 5.41 (s, 1H), 4.91 (d, J = 3 Hz, 1H), 4.72 (d, J = 3 Hz, 1H), 3.82 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (1:1 $CS_2/CDCl_3$) δ 170.16, 164.09, 158.03, 136.20, 107.43, 103.74, 85.32, 51.03, 14.68. Upon warming the samples to 0°C, all of the monomer 27 was converted into [4+2] dimers 24 and 25, [4+4] dimer 26 and polymer.

4-Carbomethoxy-2,5-dimethyl-3-furylmethyl Alcohol (22). To a stirred solution of 23.01 g (0.01084 mole) of dimethyl 2,5-dimethyl-3,4-furandicarboxylate (21) in 300 mL of dry ether ($LiAlH_4$) at 0°C, was slowly added 2.1487 g (0.0566 mole) of lithium aluminum hydride powder. After the addition was completed (ca. 40 min), the reaction mixture was stirred at room temperature for 15 h. A standard workup[77] yielded 15.37 g of crude product which was purified by column chromatography on silica gel (Baker 40-140 mesh; 320 g in a 40 mm diameter by 600 mm column) using a 30% mixture of ether in hexanes as the eluant. The first component of the product mixture which eluted from the column was starting material 21 (8.5963 g; 0.0406 mole; 37.5%). The second component which eluted from the column was 4-carbomethoxy-2,5-dimethyl-3-furylmethyl alcohol (22) (3.67 g; 0.0199 mole; 18.4%): IR (thin film) 3460, 1715, 1640, 1590, 1450, 1302, 1130, 1005 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.45 (m, 2H), 3.85 (s, 3H), 3.72 (broad s, 1H), 2.47 (s, 3H), 2.22 (s, 3H); high resolution mass spectrum calcd for $C_9H_{12}O_4$ 184.07356, measured 184.07309. Although there was ^1H NMR evidence for the presence of 3,4-bis(hydroxymethyl)-2,5-dimethylfuran (23) in the crude product mixture, 23 did not elute from the column with the six liters of solvent that were used.

4-Carbomethoxy-2,5-dimethyl-3-furylmethyl Acetate (28). A solution of 1.1236 g (0.0143 mole) of acetyl chloride in 15 mL of dry ether ($LiAlH_4$) was added dropwise to a stirred solution of 2.3893 g (0.0130 mole) of alcohol 22 and 1.9846 g (0.0196 mole) of triethylamine in 40 mL of dry ether.

After the mixture was stirred for 12 h at room temperature, 15 mL of water was added and stirring was continued for 1.5 h. The layers were separated and the aqueous layer was extracted with ether (3 x 10 mL). The ether layers were combined and then washed with water (3 x 25 mL), 1 M hydrochloric acid (3 x 10 mL), saturated sodium bicarbonate (3 x 25 mL) and saturated sodium chloride (2 x 25 mL). After the organic layer was dried ($MgSO_4$), the solvent was removed giving the crude product mixture (2.7508 g; 0.01216 mole; 94%) which was purified by short-path distillation yielding 2.4107 g (0.01066 mole; 82%) of a colorless, liquid sample of **28**: bp 75°C (0.01 mm); IR (thin film) 1745, 1725, 1600, 1450, 1235, 1140, 1090, 805, 785 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.95 (s, 2H), 3.68 (s, 3H), 2.41 (s, 3H), 2.18 (s, 3H), 1.94 (s, 3H); high resolution mass spectrum calcd for $C_{11}H_{14}O_5$ 226.08413, measured 226.08437.

Pyrolysis of 4-Carbomethoxy-2,5-dimethyl-3-furylmethyl Acetate (**28**). A 0.2311 g (0.00102 mole) quantity of **28** was pyrolyzed at 630°C and 10^{-5} Torr using the general procedure. During the pyrolysis, a solution of 1.0688 g (0.01056 mole) of triethylamine in 20 mL of carbon disulfide was deposited into the product trap. After the apparatus was shut down under nitrogen, the trap was warmed to -78°C and 15 mL of carbon disulfide at -78°C was used to rinse the trap contents to the bottom. The temperature of the product solution was slowly raised to -8°C over a 14 h period. After warming the mixture to room temperature and removing the solvent, the product residue was dissolved in ether and washed with distilled water (2 x 25 mL), 1 M hydrochloric acid (3 x 5 mL), 1 M sodium bicarbonate (3 x 25 mL) and saturated sodium chloride (2 x 25 mL). After the organic layer was dried ($MgSO_4$), the solvent was removed giving the crude product mixture which was then dissolved in a deuterochloroform solution containing 0.0170 g (0.1013 mole) of 1,1,2,2-tetrachloroethane as an internal standard. Quantitative ^{1}H NMR analysis indicated that the mixture consisted of [4+2] dimers 24 and 25 (0.0691 mole; 13.52%) and [4+4] dimer 26 (0.04337 mole; 8.54%). The ^{1}H NMR spectra of mixtures of 24, 25, and 26 formed from acetate 28 were identical to the spectra recorded for mixtures of the same compounds formed from benzoate 20.

Methyl 2,4-Dimethyl-3-furoate (30). The procedure used was based on a literature procedure for preparing ethyl 2,4-dimethyl-3-furoate.[78] Dry hydrogen chloride was bubbled intermittently into a mixture comprised of freshly distilled samples of methyl acetoacetate (178.20 g; 1.535 mole) and chloroacetone (277.11 g; 2.995 mole) over a 24 h period at temperatures from -5 to 5°C. The mixture was then poured over one liter of cracked ice in a four liter beaker and 40 g of sodium carbonate were added in small portions to neutralize the hydrochloric acid present. The layers were separated and the aqueous layer was extracted with ether (8 x 100 mL). The ether and organic layers were combined and then washed with water (1 x 100 mL), saturated sodium bicarbonate (8 x 100 mL) and saturated sodium chloride (3 x 100 mL). After the organic layer was dried over magnesium sulfate, the ether solution at 0°C was treated with 428.20 g (4.23 mole) of triethylamine. A white precipitate of triethylammonium chloride separated from solution almost immediately after the addition was completed. The mixture was stirred for 12 h at 0°C and then for 40 h at room temperature. After the addition of 300 mL of distilled water, the layers were separated and the aqueous layer was extracted with ether (5 x 50 mL). The ether layers were combined and then washed with enough 2 M hydrochloric acid to make the washings acidic (1500 mL total). The organic layer was then washed with saturated sodium bicarbonate (4 x 100 mL) and saturated sodium chloride (3 x 100 mL). After the organic layer was dried ($MgSO_4$), the solvent was removed giving the crude product mixture which was purified by two distillations through a 25 cm by 10 mm diameter column packed with glass helices, yielding 59.58 g (0.386 mole; 25.18%) of methyl 2,4-dimethyl-3-furoate (**30**): bp 60-63°C (0.8 mm); IR (thin film) 1720, 1615, 1565, 1405, 1300, 1275, 1255, 1100, 995, 800, 780, 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.07 (m, 1H), 3.78 (s, 3H), 2.46 (s, 3H), 2.07 (d, J = 1.5 Hz, 3H).

*4-Carbomethoxy-3,5-dimethylfurfuryl Chloride (**29**).* Dry hydrogen chloride was passed into a stirred mixture of 24.5134 g (0.159 mole) of methyl 2,4-dimethyl-3-furoate (**30**), 4.98 g (0.166 mole) of paraformaldehyde and 150 mL of methylene chloride at room temperature. The temperature was maintained between 22 and 35°C by intermittent cooling. The mixture was stirred at room temperature until all of the paraformaldehyde had dissolved (ca. 45 min). The dark reaction mixture was poured into ice water and after the ice had melted, the layers were separated. The aqueous layer was extracted with methylene chloride (3 x 25 mL). The methylene chloride layers were combined and then washed with water (3 x 25 mL) and saturated sodium chloride (3 x 25 mL). After the organic layer was dried ($NaHCO_3$), the solvent was removed giving the crude product (30.3186 g; 0.1496 mole; 94%) which was purified by sublimation at 45°C (0.01 mm) yielding **29**: IR ($CHCl_3$) 1730, 1650, 1595, 1405, 1115, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.53 (s, 2H), 3.77 (s, 3H), 2.48 (s, 3H), 2.10 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 164.69 (s), 160.03 (s), 144.54 (s), 120.75 (s), 114.47 (s), 51.09 (q, J = 146.92 Hz), 35.81 (t, J = 152.59 Hz), 14.36 (q, J = 129.8 Hz), 9.97 (q, J = 128.99 Hz); high resolution mass spectrum calcd for $C_9H_{11}ClO_3$ 202.03968, measured 202.03975.

Pyrolysis of 4-Carbomethoxy-3,5-dimethylfurfuryl chloride (29). Pyrolyses were carried out with ca. 0.2 g of 29 at temperatures of 660, 670, 700, 750 and 800°C and pressures of ca. 10^{-2} Torr using the general procedure. Carbon disulfide (15 mL) at -78°C was deposited into the trap during each pyrolysis. Solid sodium carbonate was added to the sample compartment and the product trap to neutralize the hydrochloric acid byproduct. After the apparatus was shut down under nitrogen, 15 mL of carbon disulfide at -78°C was used to wash the materials on the trap insert to the bottom. After ca. 10 min at -78°C, the product solution was maintained at 0°C for 10 h. After the solution was warmed to room temperature and then dried over sodium carbonate, the solvent was removed yielding the crude product mixture. Starting material was recovered at pyrolysis temperatures up to 750°C. Under all pyrolysis conditions, decomposed starting material and polymer were the major products formed. There was no evidence for the formation of monomer 27, oligomers of 27, or 2,5-bis(methylene)-3-carbomethoxy-2,5-dihydro-4-methylfuran from pyrolyses of 29.

3,4-Bis(hydroxymethyl)-2,5-dimethylfuran (23). To a stirred slurry of 4.9208 g (0.1297 mole) of lithium aluminum hydride in 150 mL of dry ether ($LiAlH_4$) at 0°C was slowly added a solution of 15.0557 g (0.0627 mole) of diethyl 2,5-dimethyl-3,4-furandicarboxylate[74-76] in 100 mL of dry ether. After the addition was completed, the mixture was stirred for 3 h at room temperature. A standard workup[77] yielded 8.57 g (0.0549 mole; 88%) of diol 75: IR ($CHCl_3$) 3610, 3395, 3060-2800, 1612, 1163, 1095, 996 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.38 (s, 4H), 3.89 (broad s, 2H), 2.20 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 146.67 (s), 118.77 (s), 54.96 (t, J = 142.83 Hz), 11.13 (q, J = 128.16 Hz).

2,5-Dimethyl-4-hydroxymethyl-3-furylmethyl Acetate (31). A solution of 3.8804 g (0.0494 mole) of acetyl chloride in 50 mL of dry ether ($LiAlH_4$) was added dropwise to a stirred solution of 7.72 g (0.0494 mole of diol 23 and 7.5196 g (0.0743 mole) of triethylamine in 75 mL of dry ether. After stirring the mixture for 5 h at room temperature, 25 mL of distilled water was added and the layers were separated. The aqueous layer was extracted with ether (3 x 25 mL). The ether layers were combined and washed with distilled water (3 x 25 mL), 1 M hydrochloric acid (3 x 25 mL), saturated sodium bicarbonate (3 x 25 mL) and saturated sodium chloride (2 x 25 mL). After the organic layer was dried ($MgSO_4$), the solvent was removed yielding the crude product mixture which was purified by column chromatography on silica gel using a 20% mixture of ethyl acetate in hexanes as the eluant. The first component which eluted from the column was 3,4-bis-(acetoxymethyl)-2,5-dimethylfuran (32) (2.5248 g; 0.01051 mole; 21.3%): bp 94°C (0.05 mm); IR (thin film) 1740, 1606, 1225, 1166, 1015, 954, 762 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.92 (s, 4H), 2.28 (s, 6H), 2.06 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 170.70 (s), 149.52 (s), 114.80 (s), 56.83 (t, J = 147.7 Hz), 20.86 (q, J = 129.4 Hz), 11.43 (q, J = 128.2 Hz); high resolution mass spectrum calcd for $C_{12}H_{16}O_5$ 240.09978, measured 240.100439. The second component which eluted from the column was 2,5-dimethyl-4-hydroxymethyl-3-furylmethyl acetate (31) (1.7620 g; 0.00889 mole; 18%): IR (thin film) 3430, 1740, 1605, 1280, 1238, 1164, 1020, 995, 960, 915, 822, 763 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.95 (s, 2H), 4.42 (s, 2H), 2.25 (s, 6H), 2.03 (s, 3H). The third component which eluted from the column was starting diol 23 (0.656 g; 0.0042 mole; 8.5%).

2,5-Dimethyl-4-trimethylsiloxymethyl-3-furylmethyl Acetate (34). A solution of 0.9692 g (0.00892 mole) of chlorotrimethylsilane in 20 mL of dry ether ($LiAlH_4$) was added dropwise to a stirred solution of 1.3649 g (0.00689 mole) of 31 and 1.4707 g (0.0153 mole) of triethylamine in 25 mL of dry ether. After the mixture was stirred for 12 h at room temperature, 10 mL of distilled water was added and the layers were separated. The aqueous layer was extracted with ether (3 x 10 mL). The ether layers were combined and then washed with 1 M hydrochloric acid (3 x 5 mL), 1 M sodium bicarbonate (2 x 5 mL) and saturated sodium chloride (3 x 10 mL). After the organic layer was dried ($MgSO_4$), the solvent was removed giving the crude product mixture which was purified by short-path distillation, yielding 1.6848 g (0.0062 mole; 90%) of 34: bp 62-63°C (0.01 mm); IR (thin film) 1738, 1604, 1244, 1224, 1163, 1045, 1013, 866, 834, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.95 (s, 2H), 4.45 (s, 2H), 2.25 (s, 6H), 2.06 (s, 3H), 0.16 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 170.92, 149.36, 147.03, 118.59, 114.63, 57.15, 55.31, 20.96, 11.48, -0.54; high resolution mass spectrum calcd for $C_{13}H_{22}O_4Si$ 270.12874, measured 270.12891.

*Pyrolysis of 2,5-Dimethyl-4-trimethylsiloxymethyl-3-furylmethyl Acetate (**34**).* Samples of **34** (ca. 0.22 g) were pyrolyzed at temperatures of 510, 550 and 580°C and at pressures of ca. 10^{-4} Torr using the general procedure. The pyrolysis products were collected in 3 mL of a 1 : 1 mixture of carbon disulfide and deuterochloroform at -78°C. ^{1}H NMR spectra of the product solutions were recorded at -60°C and at ambient temperature. Under all pyrolysis and workup conditions, the major products formed were polymeric materials and decomposition products from **34**. There was no evidence for the formation of either 2,3-bis(methylene)-2,3-dihydro-5-methyl-4-trimethylsiloxymethylfuran (**38**) or oligomers of **38** under the pyrolysis conditions.

*2,5-Dimethyl-4-trimethylsiloxymethyl-3-furylmethyl benzoate (**35**).* A solution of 8.8543 g of benzoyl chloride in 50 mL of dry ether was added dropwise to a stirred mixture of 9.64 g (0.0617 mole) of diol **23** and 9.0807 g (0.0897 mole) of triethylamine in 250 mL of dry ether. After the mixture was stirred for 34 h at room temperature, 50 mL of distilled water was added and the resulting mixture was stirred for 1 h. The layers were separated and the aqueous layer was extracted with ether (2 x 25 mL). The ether layers were combined and then washed with distilled water (2 x 50 mL), 1 M hydrochloric acid (3 x 30 mL), saturated sodium bicarbonate (3 x 25 mL) and saturated sodium chloride (2 x 25 mL). After the organic layer was dried ($MgSO_4$), the solvent was removed yielding the crude product mixture (14.7404 g) which was used without purification in the next synthetic step. A solution of 7.8726 g (0.0725 mole) of chlorotrimethylsilane in 40 mL of dry ether was added dropwise to a stirred solution of the crude product mixture obtained above (14.7404 g), and 9.23 g (0.0912 mole) of triethylamine in 250 mL of dry ether. After the mixture was stirred for 11 h at room temperature, 25 mL of distilled water was added and the layers were separated. The aqueous layer was extracted with ether (2 x 10 mL). The ether layers were combined and then washed with distilled water (3 x 25 mL), 1 M hydrochloric acid (3 x 30 mL), saturated sodium bicarbonate (2 x 25 mL) and saturated sodium chloride (2 x 25 mL). After the organic layer was dried ($MgSO_4$), the solvent was removed giving the crude product mixture which was initially purified by selective crystallization of dibenzoate **37** from a concentrated ethereal solution. Recrystallization of the white powder in ether yielded colorless prisms of **37**: mp 97-97.5°C. The IR and ^1H NMR spectral data, as well as the melting point, obtained for **37** matched the data for a sample of **37** obtained as a byproduct in the synthesis of **20**. The remainder of the crude product was purified by short-path distillation yielding four fractions. Fractions one and two consisted of 3,4-bis(trimethylsiloxymethyl)-2,5-dimethylfuran (36) (0.9847 g; 0.0033 mole; 5.3%): bp 56-85°C (0.01 mm); IR (thin film) 1605, 1282, 1250, 1165, 1055, 870, 840, 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.47 (s, 4H), 2.2 (s, 6H), 0.14 (s, 18H). Fraction 3 consisted of 2,5-dimethyl-4-trimethylsiloxymethyl-3-furylmethyl benzoate (35) (7.7602 g; 0.0233 mole; 37.83%): bp 118-132°C (0.01 mm); IR (thin film) 1715, 1600, 1265, 1245, 1170, 1100, 1155, 1020, 914, 866, 834, 740, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.22-7.95 (m, 2H), 7.62-7.2 (m, 3H), 5.25 (s, 2H), 4.07 (s, 2H), 2.34 (s, 3H), 2.26 (s, 3H), 0.14 (s, 9H). The fourth fraction consisted of dibenzoate 37 (1.5407 g). The total yield of 37 obtained from crystallization and distillation was 4.6018 g (0.0126 mole; 20.47%).

Pyrolysis of 2,5-Dimethyl-4-trimethylsiloxymethyl-3-furylmethyl Benzoate (35). A 0.03064 g quantity of 35 was pyrolyzed at 580°C and 10^{-5} Torr using the general procedure. During the pyrolysis, 25 mL of carbon disulfide at -78°C was distilled into the product trap. After the apparatus was shut down under nitrogen, the product trap was warmed to -78°C and 10 mL of carbon disulfide was used to rinse the trap contents to the bottom. After the mixture was stirred for 1 h at -78°C, its temperature was raised to room temperature. The insert of the trap was lined with a large amount of a colorless, polymeric film. The product solution was dried over sodium carbonate and concentrated, yielding the product residue. There was no NMR spectral evidence for the presence of either 2,3-bis(methylene)-2,3-dihydro-5-methyl-4-trimethylsiloxymethylfuran (38) or any oligomers of 38 in the product mixture.

Pyrolysis of 3,4-Bis(trimethylsiloxymethyl-2,5-dimethylfuran (36). A 0.2185 g quantity of 36 was pyrolyzed at 570°C and 10^{-5} Torr using the general procedure. The pyrolysis products were collected in 10 mL of carbon disulfide and after the solution was stirred for 1 h at -78°C, its temperature was slowly raised to room temperature. The product trap contained a substantial amount of pink, polymeric material. The product solution was dried over magnesium sulfate and concentrated, giving the crude product mixture. A ^{1}H NMR spectrum of the mixture indicated that a substantial amount of 36 was converted into diol 23 and 2,5-dimethyl-4-trimethylsiloxymethyl-3-furylmethyl alcohol (39).

4,4'-Bis(acetoxymethyl)-5,5'-dimethyl-[2.2](2,3)furanophane (40). To a stirred slurry of 0.0847 g (2.33 mmole) of lithium aluminum hydride in 5 mL of dry tetrahydrofuran ($LiAlH_4$) at 0°C was slowly added a solution of 0.1296 g

(0.3899 mole) of 4,4'-bis(carbomethoxy)-5,5'-dimethyl-[2.2]-(2,3)furanophane (26) in 10 mL of dry tetrahydrofuran (THF). After the mixture was stirred for 5.5 h at room temperature, a standard workup[77] yielded 0.0934 g (0.338 mmole; 87%) of 33 as a white powder: mp 160-300°C (dec.). Without purification, 33 was converted into its diacetate derivative 40. A solution of 0.0552 g (0.7032 mmole) of acetyl chloride in 2 mL of dry THF was added dropwise to a stirred solution of diol 33 (0.0934 g; 0.338 mmole) and 0.2473 g (2.44 mmole) of triethylamine in 15 mL of dry THF. After the mixture was heated to its reflux temperature for 11 h, 10 mL ether and 2 mL of distilled water were added and the layers were separated. The aqueous layer was extracted with ether (3 x 10 mL). The ether layers were combined and then washed with 1 M hydrochloric acid (3 x 5 mL), 1 M sodium bicarbonate (2 x 5 mL) and saturated sodium chloride (3 x 5 mL). After the organic layer was dried ($MgSO_4$), the solvent was removed yielding 0.105 g of diacetate 40 (0.2913 mmole; 92%) which was isolated as a white powder: IR ($CHCl_3$) 1733, 1645, 1602, 1235, 1022, 955 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.84 (s, 4H), 3.02 (s, 4H), 2.75 (s, 4H), 2.22 (s, 6H), 2.04 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 170.92, 148.93, 148.11, 118.26, 115.39, 56.99, 25.73, 22.37, 21.02, 11.54; GLC/MS (70 eV) m/e (relative intensity) 362.12 (0.07), 361.16 (0.59), 360.10 (2.78), 300.10 (3.42), 240.04 (14.00), 180.04 (9.93), 121.06 (36.04), 120.04 (100.00), 91.02 (10.70), 60.00 (11.44); GLC/MS (18 eV) m/e (relative intensity) 362.10 (2.64), 361.12 (16.33), 360.10 (71.94), 301.10 (13.78), 300.00 (58.72), 258.06 (24.47), 257.04 (26.50), 241.06 (18.94), 240.06 (100.00), 180.04 (4.72), 120.04 (13.10), 60.00 (16.31); high resolution mass spectrum calculated for $C_{20}H_{24}O_6$ 360.15730, measured 360.15772.

Pyrolysis of 4,4'-Bis(acetoxymethyl)-5,5'-dimethyl-[2.2](2.3)furanophane (40). A 0.0328 g (0.091 mmole) sample of 40 was pyrolyzed at 580°C and 10^{-5} Torr using the general procedure. During the pyrolysis, 2 mL of a 1 : 1 mixture of carbon disulfide and deuterochloroform at -78°C was distilled into the product trap. After the reaction was stopped and the product mixture was warmed to -78°C, 2 mL of the solvent mixture at -78°C were used to rinse the material on the walls of the trap to the bottom. A substantial amount of insoluble, polymeric material was present among the pyrolysis products. ^1H NMR spectra were recorded at -65, -50, -25, 0 and 25°C. At temperatures below -25°C, the signals observed in the spectra were broad and poorly resolved. The spectra obtained at -25 and 0°C included signals which could be assigned to furanoradialene (42) and the [4+2] dimer 41 of 42. For furanoradialene (42): ^1H NMR (1:1 $CS_2/CDCl_3$; 0°C) δ 5.56 (broad s, 4H), 4.59

(m, 2H), 4.52 (m, 2H) [lit.[72] ^{1}H NMR ($CDCl_3$; -50°C) δ 5.59 (broad s, 4H), 4.61 (AB pattern, J = 2.5 Hz, 4H)]. For [4+2] dimer **41**: ^{1}H NMR (1:1 $CS_2/CDCl_3$; 0°C) δ 5.56 (broad s, 1H), 4.94 (s, 1H), 4.59 (m, 1H), 4.52 (m, 4H), 4.12 (m, 2H), 3.95 (m, 1H), 3.3-0.7 (broad region of overlapping multiplets, 6H) [lit.[79] ^{1}H NMR (1:1 $CS_2/CDCl_3$) δ 5.5 (s, 1H), 4.92 (s, 1H), 4.54 (d, J = 2.5 Hz, 1H), 4.46 (d, J = 2.5 Hz, 4H), 4.09 (m, 2H), 3.94 (m, 1H), 2.55-2.27 (m, 4H), 1.88-1.65 (m, 2H). Warming the sample to room temperature resulted in decreases in the areas of the signals at δ 5.56 and 4.59, indicating a decrease in the concentration of furanoradialene (**42**). A corresponding increase in the areas of the signals at δ 4.94, 4.12 and 3.95 indicated an increase in the concentration of the [4+2] dimer **41** of **42**. The limited amounts of diacetate **40** available were insufficient to quantify the amounts of furanoradialene **42** and [4+2] dimer **41** present in the product mixture.

REFERENCES

1. Cram, D. J.; Steinberg, H. J. Am. Chem. Soc. 1951, 73, 5691.
2. Boekelheide, V. Acc. Chem. Res. 1980, 13, 65.
3. Vögtle, R.; Hohner, G. Top. Curr. Chem. 1978, 74, 1.
4. Misumi, S.; Otsubo, T. Acc. Chem. Res. 1978, 11, 251.
5. Cram, D. J.; Hornby, R. B., Truesdale, E. A.; Reich, H. J.; Delton, M. H.; Cram, J. M. Tetrahedron 1974, 30, 1757.
6. Vögtle, F.; Neumann, P. Synthesis 1973, 85.
7. Vögtle, F.; Neumann, P. Angew. Chem. Int. Ed. Engl. 1972, 11, 73.
8. Cram, D. J.; Cram, J. M. Acc. Chem. Res. 1971, 4, 204.
9. Smith, B. H. "Bridged Aromatic Compounds"; Academic Press: New York, 1964.
10. Griffin, R. W., Jr. Chem. Rev. 1963, 63, 45.
11. Vögtle, F.; Neumann, P. Tetrahedron 1970, 26, 5847.
12. Boekelheide, V.; Ewing, G. Tetrahedron Lett. 1978, 4245.
13. Cava, M. P.; Deana, A. A. J. Am. Chem. Soc. 1959, 81, 4266.
14. Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie GmbH: Weinheim, Germany, 1971; p 82.
15. Hart, H.; Fish, R. W. J. Am. Chem. Soc. 1960, 82, 749.
16. Hart, H.; Hartlage, J. A.; Fish, R. W.; Rafos, R. R. J. Org. Chem. 1966, 31, 2244.
17. Loudon, A. G.; Maccoll, A.; Wong, S. K. J. Chem. Soc. (B) 1970, 1733.

18. Loudon, A. G.; Maccoll, A.; Wong, S. K. J. Am. Chem. Soc. 1969, 91, 7577.

19. Gray, R.; Harruff, L. G.; Krymowski, J.; Peterson, J.; Boekelheide, V. J. Am. Chem. Soc. 1978, 100, 2892.

20. Schiess, P.; Heitzmann, M. Helv. Chim. Acta 1978, 61, 844.

21. Schiess, P.; Heitzmann, M.; Rutschmann, S.; Staheli, R. Tetrahedron Lett. 1978, 4569.

22. Morello, M. J.; Trahanovsky, W. S. Tetrahedron Lett. 1979, 4435.

23. Jensen, F. R.; Coleman, W. E.; Berlin, A. J. Tetrahedron Lett. 1962, 15.

24. Aalbersberg, W. G. L.; Vollhardt, K. P. C. Tetrahedron Lett. 1979, 1939.

25. Ewing, G. D.; Boekelheide, V. Chem. Commun. 1979, 207.

26. Sekine, Y.; Brown, M.; Boekelheide, V. J. Am. Chem. Soc. 1979, 101, 3126.

27. Kleinschroth, J.; Hopf, H. Angew. Chem. Intl. Ed. Engl. 1979, 18, 329.

28. Schirch, P. F. T.; Boekelheide, V. J. Am. Chem. Soc. 1979, 101, 3125.

29. Sekine, Y.; Boekelheide, V. J. Am. Chem. Soc. 1981, 103, 1777.

30. Trahanovsky, W. S.; Cassady, T. J.; Woods, T. L. J. Am. Chem. Soc. 1981, 103, 6691.

31. Winberg, H. E.; Fawcett, F. S.; Mochel, W. E.; Theobald, C. W. J. Am. Chem. Soc. 1960, 82, 1428.

32. Cram, D. J.; Montgomery, C. S.; Knox, G. R. J. Am. Chem. Soc. 1966, 88, 515.

33. Wasserman, H. H.; Keehn, P. M. Tetrahedron Lett. 1969, 3227.

34. Wynberg, H.; Helder, R. Tetrahedron Lett. 1971, 4317.

35. Fletcher, J. R.; Sutherland, I. O. Chem. Commun. 1969, 1504.

36. Gault, I.; Price, B. J.; Sutherland, I. O. Chem. Commun. 1967, 540.

37. Mizogami, S.; Otsubo, T.; Sakata, Y.; Misumi, S. Tetrahedron Lett. 1971, 2791.

38. Mizogami, S.; Osaka, N.; Otsubo, T.; Sakata, Y.; Misumi, S. Tetrahedron Lett. 1974, 799.

39. Osaka, N.; Mizogami, S.; Otsubo, T.; Sakata, Y.; Misumi, S. Chem. Lett. 1974, 515.

40. Hammond, P. S.; Longone, D. T. Tetrahedron Lett. 1978, 415.

41. Wong, C. and Paudler, W. W. J. Org. Chem. 1974, 39, 2570.

42. Wasserman, H. H.; Bailey, D. T. Chem. Commun. 1970, 107.

43. Mahaffey, R. L.; Atwood, J. L.; Humphrey, M. B.; Paudler, W. W. J. Org. Chem. 1976, 41, 2963.

44. Haley, J. F., Jr.; Rosenfeld, S. M.; Keehn, P. M. J. Org. Chem. 1977, 42, 1379.

45. Mashraqui, S. H.; Keehn, P. M. J. Am. Chem. Soc. 1982, 104, 4461.

46. Staab, H. A.; Appel, W. K. Liebigs Ann. Chem. 1981, 1065.

47. Kang, H. C.; Boekelheide, V. Angew. Chem. Int. Ed. Engl. 1981, 20, 571.

48. Grummitt, O.; Splitter, J. J. Am. Chem. Soc. 1952, 74, 3924.

49. Grummitt, O.; Mandel, Z. J. Am. Chem. Soc. 1956, 78, 1054.

50. Bailey, W. J.; Goossens, J. C. J. Am. Chem. Soc. 1956, 78, 2804.

51. Bailey, W. J.; Barclay, R., Jr. *J. Org. Chem.* 1956, 21, 328.

52. a) Greenwood, F. L. *J. Org. Chem.* 1959, 24, 1735.

    b) Greenwood, F. L. *J. Org. Chem.* 1962, 27, 2308.

53. Clauson-Kaas, N.; Elming, N. *Acta Chem. Scand.* 1952, 6, 560.

54. Trahanovsky, W. S.; Morello, M. J. "Abstracts of Papers", 178th National Meeting of the American Chemical Society, Washington, D.C., Sept. 1979, American Chemical Society: Washington, D.C., 1979; PETR 46.

55. Morello, M. J. M.S. Thesis, Iowa State University, Ames, Iowa, 1980.

56. Cristol, S. J.; Barasch, W.; Tieman, C. H. *J. Am. Chem. Soc.* 1955, 77, 583.

57. Marvel, C. S.; Brace, N. O. *J. Am. Chem. Soc.* 1948, 70, 1775.

58. Landor, P. D.; Landor, S. R. *J. Chem. Soc.* 1956, 1015.

59. Heilbron, I. M.; Jones, E. R. H.; McCombie, J. T.; Weedon, B. C. *J. Chem. Soc.* 1945, 88.

60. Burton, H. *J. Chem. Soc.* 1928, 1650.

61. Balfe, M. P.; Kenyon, J. *Trans. Faraday Soc.* 1941, 37, 721.

62. Braude, E. A.; Turner, D. W.; Waight, E. S. *J. Chem. Soc.* 1958, 2396.

63. Braude, E. A.; Turner, D. W. *J. Chem. Soc.* 1958, 2404.

64. Errede, L. A. *J. Am. Chem. Soc.* 1961, 83, 949.

65. Martin, H. D.; Mayer, B. *Tetrahedron Lett.* 1979, 2351.

66. Griffin, G. W.; Peterson, L. I. *J. Am. Chem. Soc.* 1963, 85, 2268.

67. Ito, Y.; Miyata, S.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* 1981, 103, 5250.

68. Lokensgard, D. M. Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1978.

69. Gorham, W. F. J. Polymer Sci (Part A-1) 1966, 4, 3027.

70. Yeh, Y. L.; Gorham, W. F. J. Org. Chem. 1969, 24, 2366.

71. Harruff, L. G.; Brown, M.; Bockelheide, V. J. Am. Chem. Soc. 1978, 100, 2893.

72. Jullien, J.; Pechine, J. M.; Perez, F.; Piade, J. J. Tetrahedron Lett. 1980, 21, 611.

73. Trahanovsky, W. S.; Ong, C. C.; Pataky, J. G.; Weitl, F. L.; Mullen, P. W.; Clardy, J. C.; Hansen, R. S. J. Org. Chem. 1971, 36, 3575.

74. Gardner, J. A.; Rydon, H. N. J. Chem. Soc. 1938, 45.

75. Newman, M. S.; Cella, J. A. J. Org. Chem. 1973, 38, 3482.

76. Knorr, L. Chem. Ber. 1884, 17, 2863.

77. Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. I, p 584.

78. Alexander, E. R.; Baldwin, S. J. Am. Chem. Soc. 1951, 73, 356.

79. Trahanovsky, W. S.; Cassady, T. J. Unpublished Results Department of Chemistry, Iowa State University, Ames, IA.

SUMMARY

The flash vacuum pyrolysis (FVP) chemistry of a series of methyl-substituted, furfuryl benzoates and methyl-substituted, 3-furylmethyl benzoates has been investigated. Pyrolysis of 3-methylfurfuryl benzoate gives 3-methyl-4-methylenecyclobut-2-enone and the head-to-head, [4+4] dimer of 2,3-bis(methylene)-2,3-dihydrofuran as the major products. Pyrolysis of 5-methylfurfuryl benzoate produces either 2,5-bis(methylene)-2,5-dihydrofuran or 4-methylenecyclopent-2-enone as major products, depending upon the pyrolysis temperature. Pyrolysis of 3,5-dimethylfurfuryl benzoate forms a product mixture which at -60°C consists of 2,5-bis(methylene)-2,5-dihydro-3-methylfuran and 2,3-bis(methylene)-2,3-dihydro-5-methylfuran. Warming the product mixture to room temperature resulted in the conversion of 2,3-bis(methylene)-2,3-dihydro-5-methylfuran into its head-to-head, [4+4] dimer. Mechanisms were proposed for the formation of the pyrolysis products from the methyl-substituted, furfuryl benzoates which involved either α or β eliminations of benzoic acid after one or more [3,3] shifts of the benzoate group.

The pyrolysis of 2-methyl-3-furylmethyl benzoate formed the head-to-head, [4+4] dimer of 2,3-bis(methylene)-2,3-dihydrofuran in the absence of 3-methyl-4-methylenecyclo-

but-2-enone. The initial formation of 2,3-bis(methylene)-2,3-dihydrofuran was established by trapping experiments with methyl acrylate and by recording ^{1}H and ^{13}C NMR spectra of a product solution at -60°C. A study of the pyrolysis chemistry of 2-methyl-3-furyl(dideutero)methyl benzoate established that a 1,4 elimination of benzoic acid from the starting ester had taken place. A diradical mechanism was proposed for the formation of the [4+4] dimer from 2,3-bis-(methylene)-2,3-dihydrofuran. The addition of methyl substituents to the furan ring resulted in the formation of the corresponding methyl-substituted, 2,3-bis(methylene)-2,3-dihydrofurans. A sample of 2,3-bis(methylene)-2,3-dihydro-4-methylfuran was converted into a mixture of the natural product menthofuran and its isomer isomenthofuran. The Diels-Alder reactions of 2,3-bis(methylene)-2,3-dihydrofurans thus serve as a direct method for obtaining the furanocyclohexane, ring skeleton. The reversible, chelatropic addition of sulfur dioxide to 2,3-bis(methylene)-2,3-dihydro-4-methylfuran was studied as a method of generating low concentrations of 2,3-bis(methylene)-2,3-dihydro-4-methylfuran in solution.

The pyrolysis chemistry of 3-furylmethyl benzoate was investigated in order to provide evidence supporting the proposed mechanism for the formation of the pyrolysis products from furfuryl benzoate.[1,4] Pyrolysis of 3-furylmethyl benzoate produced vinylacetylene and 4-methylenecyclobut-2-enone as the major products. A mechanism was proposed for the formation of the pyrolysis products involving an α elimination of benzoic acid after a [3,3] sigmatropic shift of the benzoate group.

Pyrolysis of diesters of 3,4-bis(hydroxymethyl)-2,5-dimethylfuran formed furanoradialene as the only major product. Warming the product solution to room temperature resulted in the conversion of furanoradialene into one [4+2] dimer.

The method of forming 2,3-bis(methylene)-2,3-dihydrofurans by the pyrolysis of 2-methyl-3-furylmethyl benzoates was used in several approaches toward the synthesis of [2.2.2.2](2,3,4,5)furanophane. The pyrolysis of 4-carbomethoxy-2,5-dimethyl-3-furylmethyl benzoate at 550°C formed 2,3-bis(methylene)-4-carbomethoxy-2,3-dihydro-5-methylfuran as the only major, nonpolymeric product. Warming the product solutions to room temperature resulted in the formation of two [4+2] dimers and the head-to-head, [4+4] dimer of 2,3-bis(methylene)-4-carbomethoxy-2,3-dihydro-5-methylfuran. The [4+4] dimer was then converted into 4,4'-bis(acetoxymethyl)-5,5'-dimethyl-[2.2](2,3)furanophane.

Pyrolysis of 4,4'-bis(acetoxymethyl)-5,5'-dimethyl-[2.2]-(2,3)furanophane under a variety of conditions resulted in the formation of complex product mixtures with furanoradialene being the only nonpolymeric product identified.

ADDITIONAL LITERATURE CITED

1. Trahanovsky, W. S.; Park, M.-G. J. Am. Chem. Soc. 1973, 95, 5412.
2. De Selms, R. C.; Delay, F. J. Am. Chem. Soc. 1973, 95, 274.
3. Cava, M. P. "Cyclobutadiene and Related Compounds"; Academic Press: New York, 1967; p 157-158.
4. Trahanovsky, W. S.; Park, M.-G. J. Org. Chem. 1974, 39, 1448.
5. Trahanovsky, W. S.; Alexander, D. L. J. Am. Chem. Soc. 1979, 101, 142.
6. Trahanovsky, W. S.; Woods, T. L. Unpublished Results Department of Chemistry, Iowa State University, Ames, IA.
7. Mc Cullough, J. J. Acc. Chem. Res. 1980, 13, 270.
8. Flynn, C. R.; Michl, J. J. Am. Chem. Soc. 1974, 96, 3280.
9. Migirdicyan, E.; Baudet, J. J. Am. Chem. Soc. 1975, 97, 7400.
10. Tseng, K. L.; Michl, J. J. Am. Chem. Soc. 1977, 99, 4840.
11. Steiner, R. P.; Miller, R. D.; Dewey, H. J.; Michl, J. J. Am. Chem. Soc. 1979, 101, 1820.
12. Errede, L. A. J. Am. Chem. Soc. 1961, 83, 949.
13. Trahanovsky, W. S.; Ong, C. C.; Pataky, J. G.; Weitl, F. L.; Mullen, P. W.; Clardy, J. C.; Hansen, R. S. J. Org. Chem. 1971, 36, 3575.
14. Trahanovsky, W. S.; Cassady, T. J.; Woods, T. L. J. Am. Chem. Soc. 1981, 103, 6691.

ACKNOWLEDGMENTS

I would like to thank Dr. Walter S. Trahanovsky, "Dr. T", for his guidance, patience and support during the course of this investigation. I would also like to thank the members of the Trahanovsky research group, during my years at Iowa State, for their friendship and experimental assistance.

I am grateful to Professor Glen A. Russell for providing me with a sample of 2-isopropylidene-4-methylcyclohexanone. I am also grateful to Professor Thomas A. Spencer for providing me with an IR spectrum of isomethofuran and an IR method for distinguishing between menthofuran and isomenthofuran. I am also grateful to Professor K. N. Houk for providing me with the results of a CNDO/2 calculation on 2,3-bis(methylene)-2,3-dihydrofuran.

I would especially like to thank my wife, Shelley, for her love, encouragement and patience throughout the time that this dissertation was written and for her assistance in typing the rough draft. I would finally like to thank Lynn Moore for typing the final draft.