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Gas phase thermal reactions: I. Propargyl esters; II. Phenyl propargyl ethers; III. Cinnamyl derivatives

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Gas phase thermal reactions:

I. Propargyl esters

II. Phenyl propargyl ethers

III. Cinnamyl derivatives

by

Patrick Walter Mullen

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES

LIST OF SCHEMES

LIST OF FIGURES

Part I. Gas phase thermal reactions: propargyl esters

INTRODUCTION

The rearrangement of propargyl esters in the condensed phase has been used for sometime as a route to allenyl esters (1-5). Upon pyrolysis at temperatures near 600° in the gas phase, we have now found that propargyl esters rearrange to 2-methylidene-1,3-propanediones in high yield. The only previous report of a propargyl ester reaction under similar conditions concerned the cleavage reaction of dipropargyl oxalate to form propargyl radicals (6). The generality of our new rearrangement reaction was explored and it was found that certain esters will ultimately decarbonylate to form simple α,β-unsaturated ketones.

Mechanistic aspects and preparative utility of the reaction were considered. There was good evidence that the rearrangement takes place <u>via</u> a sequence of concerted reactions. Several earlier reports of isolation of methylidenediones which were unsubstituted at the methylidene position (7, 8), were refuted. We believe that our synthesis is the only known route to these compounds. The reaction was also shown to be a simple, low-cost preparation of α,β-unsaturated ketones, valuable synthetic intermediates.

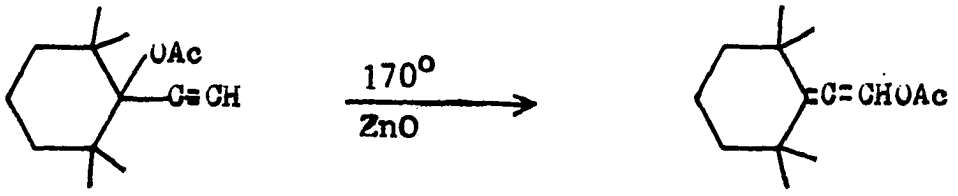
LITERATURE REVIEW

Trahanovsky and Ong (6) have recently found that uncatalyzed gas phase pyrolysis of dipropargyl oxalate produced benzene as the only isolable product:

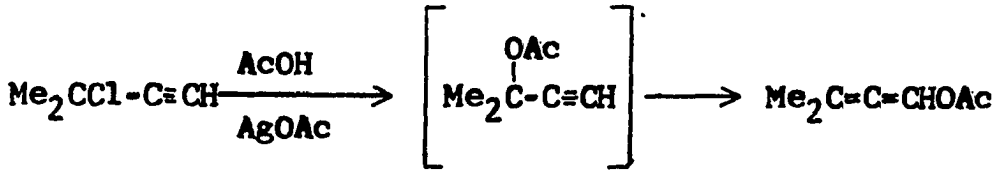
$$(HC{\equiv}C\text{-}CH_2\text{-}O\text{-}CO\text{-})_2 \xrightarrow{660^\circ} C_6H_6 + 2CO_2$$

They reported that radical formation is a general reaction of β,γ-unsaturated oxalate esters under these conditions.

The literature contains a number of references to catalyzed rearrangements of propargyl esters (1-5). 1-Ethynylcyclohexyl acetates were reported by Landor and Landor (1) to rearrange in the liquid phase at ca. 200° in the presence of zinc oxide:

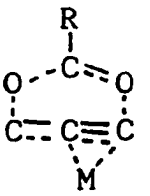


With catalysts derived from other metals, especially silver compounds, analogous reactions have been shown to occur near room temperature (2-5). While the observation by Zakharova (2) of allenyl ester formation predates the work by Landor and Landor,



the possibility that thiswas simply an S_N2' addition of acetate to the chloride has been raised (1). The scope of the silver catalyzed reaction has been extended to include the rearrangement of formates and benzoates (3), steroidal acetates (4), and as a method of producing optically active allenes from optically active propargyl acetates (4).

Mechanistically, these reactions are believed to involve a cyclic six-membered transition state (1, 4, 5) whose electronic or steric requirements are lowered in energy by metal-alkyne interaction.



No attempt has been made to rule out a 1,3 acetate shift of the metal complexed propargyl ester even though similar shifts are believed to occur in other propargyl systems, particularly the halides (7).

RESULTS

3-Phenylpropargyl acetate and benzoate

The acetate and benzoate esters of 3-phenylpropargyl alcohol were prepared by conventional means. Samples of each were allowed to vaporize slowly through a vycor tube which was filled with vycor helices. Pyrolyses temperatures ranged from 580-680°. The reaction products were then trapped in a liquid nitrogen cooled trap. The results are shown in Table 1. The nmr spectra of the crude products were quite simple, Table 2, and the impurities amounted to only five or less percent.

Table 1. Products and yields from pyrolyses of 3-phenylpropargyl acetate and benzoate

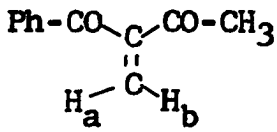
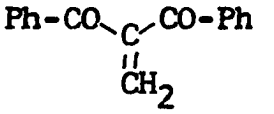
Substrate $Ph-C\equiv C-CH_2-O-CO-R$	Pyrolysis Temperature	$Ph-CO-\underset{\underset{CH_2}{\|}}{C}-CO-R$ Yield, % [a]	Residual Substrate, %
3-Phenylpropargyl acetate R=CH_3	680°	72	-
	630°	62	21
	580°	38	45
3-Phenylpropargyl benzoate R=Ph	660°	88	trace
	660°	85	-
	620°	67	4

[a] Yields determined by nmr spectroscopy using an internal standard, ethyl benzoate.

The preparation of the 1,1-dibenzoylethylene had been reported by Cannon et al. (8):

$$Ph-CO-CH_2-CO-Ph + CH_2O \xrightarrow{\text{Base}} Ph-CO-\underset{\underset{CH_2}{\|}}{C}-CO-Ph$$

Table 2. NMR spectral data for methylidenediones

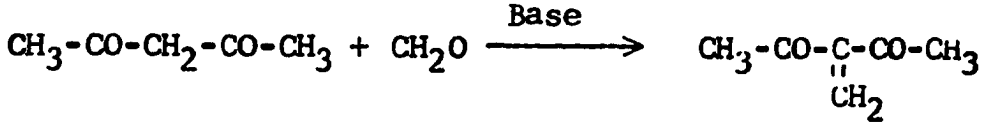
Compound	Resonance	Chemical Shift (δ)	Pattern
	CH_3	2.35	s
	H_a[a]	5.98	s
	H_b	6.40	s
	Ph[b]	7.15-7.60	m
		7.70-7.95	m
	CH_2	6.15	s
	Ph[b]	7.14-7.54	m
		7.65-7.85	m

[a]The resonance is assigned to H_a because the shift is closer to that of the diphenyl product. Slight conformational distortions may have a large effect on these shifts.

[b]The multiplets are very characteristic of a Ph-CO compound.

Upon repetition of their work, we isolated a product with the same melting point as was reported, however, it was apparent from the nmr spectrum that the reported compound was 1,1,3,3-tetrabenzoylpropane; ($CDCl_3$) δ 5.70 (t, J=7 Hz, 2, CH_2), 2.75 (t, J=7 Hz, 2, CH), 7.20-8.25 (m, 20, Ph).

We have also attempted to repeat another Knoevenagel reaction reported by Polansky and Schuster (9):



An nmr spectrum of a fraction collected at the reported boiling point indicated that the product was a complex

mixture of compounds. This reaction has been extensively studied by both Wilson (10) and O'Loane et al. (11). Both groups found only products derived from 2:1 or 3:1 condensations in the Knoevenagel reaction, consistent with our results in the dibenzoylmethane-formaldehyde condensation. These workers were able to isolate the normal 1:1 condensation products of acetylacetone and higher aldehydes:

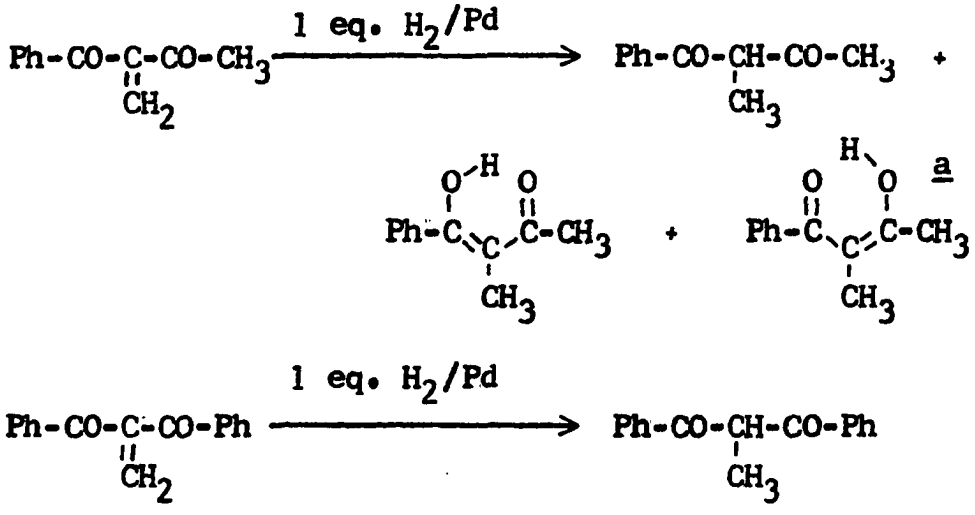
$$CH_3\text{-}CO\text{-}CH_2\text{-}CO\text{-}CH_3 + CH_3\text{-}CHO \xrightarrow{\text{Base}} CH_3\text{-}CO\text{-}\underset{\underset{H\text{-}C\diagdown CH_3}{\|}}{C}\text{-}CO\text{-}CH_3$$

In order to further establish the methylidenediones as reasonable intermediates in the formation of these 2:1 condensation products, and in order to further establish the identity of our product, we reacted some dibenzoylmethane with our 1,1-dibenzoylethylene:

$$(Ph\text{-}CO)_2CH_2 + (Ph\text{-}CO)_2CH{=}CH_2 \xrightarrow{\text{Base}} (Ph\text{-}CO)_2CH\text{-}CH_2\text{-}CH(CO\text{-}Ph)_2$$

The product nmr spectrum and melting point were identical to those of the 1,1,3,3-tetrabenzoylpropane product from our Knoevanagel reaction. Further evidence for the methylidenedione structures, obtained by hydrogenation and ir, is summarized in Table 3 and Table 4, respectively.

Table 3. Hydrogenation of methylidenediones

Compound	Product
	

[a]All tautomeric forms found in nmr spectrum. The enol forms could not be distinguished in the spectrum.

Table 4. Infrared spectral data of methylidenediones

Compound	Phase	Adsorptions
Ph-CO-C(=CH$_2$)-CO-CH$_3$	(neat) cm^{-1}	1735(m), 1660 (s, broad), 1594(m)
Ph-CO-C(=CH$_2$)-CO-Ph	(CCl_4) cm^{-1}	1731(m), 1683 (shoulder), 1675(s), 1667 (s), 1583(m)

3-Phenylpropargyl formate, propargyl benzoate, 1-phenylpropargyl acetate, propargyl cyclohexanecarboxylate and propargyl acetate

Upon pyrolysis of these esters under the same conditions as our previously mentioned propargyl esters the main products were found to be α,β-unsaturated ketones, Table 5.

Table 5. Yields of α,β-unsaturated ketones formed from pyrolyses of propargyl esters

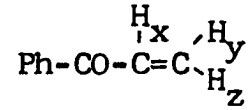
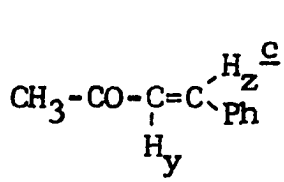
Substrate	Pyrolysis Temperature	Product	Yield,%	Residual Substrate,%
Ph-C≡C-CH_2-O-CO-H	670°	Ph-CO-CH=CH_2	94[a]	trace
	640°		82	16
3-Phenylpropargyl formate	560°		34	55
HC≡C-CH_2-O-CO-Ph	660°	Ph-CO-CH=CH_2	80	3
	640°		82	8
Propargyl benzoate				
HC≡C-CH(Ph)-O-CO-CH_3	645°	CH_3-CO-CH=C(H)-Ph	79	7
	640°		87	7
	670°		48	4
1-Phenylpropargyl acetate				
HC≡C-CH_2-O-CO-C_6H_{11}	630°	C_6H_{11}-CO-CH=CH_2	54	11
	630°		56	10
Propargyl cyclohexane-carboxylate				
HC≡C-CH_2-O-CO-CH_3	630°	CH_3-CO-CH=CH_2	60	trace
Propargyl acetate				

[a]Yields were determined by nmr spectroscopy with ethyl benzoate or propiophenone used for an internal standard.

The products were identified by their nmr spectra, Table 6, which, with the exception of cyclohexyl vinyl ketone, were compared with spectra of commercial samples or published data.

In addition to this, the ir spectrum of phenyl vinyl ketone, (neat) cm^{-1} 1673 (s), 1665 (s), 1608 (s) was found to be consistent with published data (12). Upon addition of

Table 6. NMR spectral data of α,β-unsaturated ketone products

Compound	Resonance	Chemical Shift, δ	Pattern	Coupling, Hz
	H_y	5.89	d of d	J_{yx}=10.4 J_{yz}=2.4
	H_z	6.44	d of d	J_{zx}=17.0[a] J_{yz}=2.4
	H_x	7.3[b]		
	Ph	7.23-7.68 7.85-8.11	m m	
	H_y	6.60	d	J_{yz}=16
	H_z[b]	7.41		
	CH_3	2.26	s	
	Ph	7.10-7.67	m	
CH_3-CO-CH=CH_2[d]	CH_3	2.20	s	
	CH-CH_2	5.70-5.98 6.12-6.35	m m	
CycloC_6H_{11}-CO-CH=CH_2	C_6H_{11}	1.1-2.3	m	
	CH-CH_2	5.52-5.75[e] 5.95-6.65	m m	

[a]The published value for this coupling is 18.4 (13) for a spectra recorded on a 40 MHz machine.

[b]The pattern was partially obscured by the aromatic hydrogen resonances.

[c]Spectrum #251, High Resolution NMR Spectra Catalog, vol. 1, Varian Associates, Palo Alto, Calif., 1962.

[d]Aldrich Chemical Co.

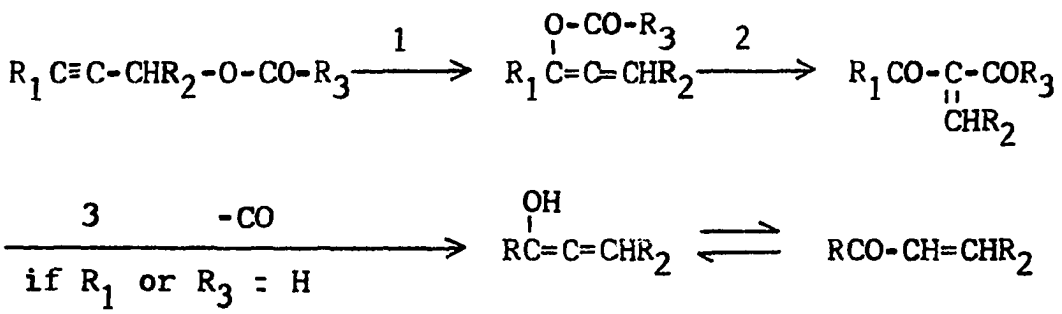
[e]Pattern very similar to the same region of methyl vinyl ketone spectra.

one equivalent hydrogen to it, propiophenone was recovered and identified by comparison of its nmr and ir spectra with those of an authentic sample (Eastman Organic Chemicals).

DISCUSSION

3-Phenylpropargyl acetate, benzoate, and formate, propargyl cyclohexanecarboxylate and acetate

We postulate that all the propargyl esters react via the basic mechanism shown in Scheme 1. The precedent for step 1, the previously discussed metal catalyzed rearrangements, is well documented.



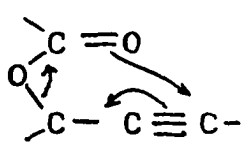
R_1 = H, Ph

R_2 = H, Ph

R_3 = H, Ph, Me, Cyclohexyl

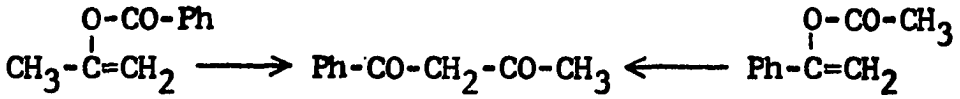
Scheme 1. Mechanism proposed for propargyl ester rearrangement

Our experimental conditions (no solvent or metal catalysts) would also be conducive to Claisen type reactions:



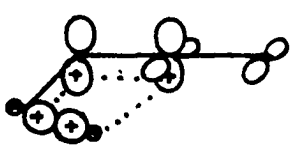
Step 2 involves a 1,3 acyl shift common for vinyl esters at temperatures between 500° and 600° in the gas phase (14, 15)

and has been used in the commercial preparation of acetylacetone (14).

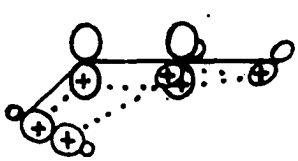


Because their yields depended on the extent to which the pyrolysis tube was conditioned, Young et al. (15) assumed that this acyl shift was a surface reaction. This is, however, insufficient evidence for their conclusion and no further attempt has been made to prove or disprove the possibility of a surface reaction.

We would like to also consider the possible concerted reaction paths for the allenyl ester rearrangements. The reaction is thermally allowed as either proceeding through a 4 electron, 1 sign inversion transition state (16);

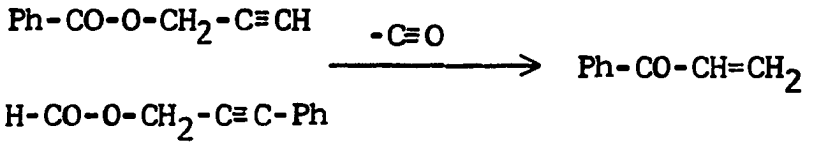


or as a 6 electron ($\sigma 2s, \pi 2s, \pi 2s$) cycloaddition (17);

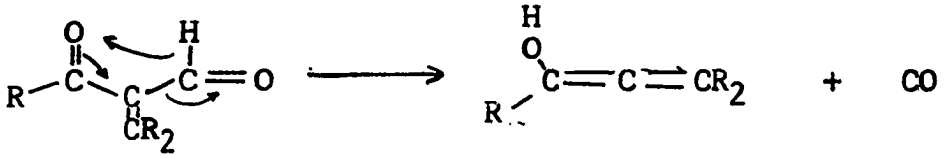


Because of our high yields and experimental conditions, we favor the concerted mechanisms. From consideration of the

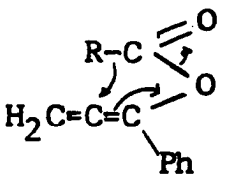
fact that both phenylpropargyl formate and propargyl benzoate form the same pyrolysis product,



we believe the decarbonylation step most reasonably involves hydrogen transfer to an oxygen:

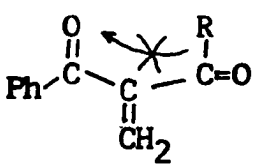


The other possibility, transfer to the central allenyl carbon atom of the intermediate ester would require that the hydrogen atom and the other substituents, such as the phenyl or methyl group, migrate with comparable facility:



R = H, CH_3, Ph

The migratory aptitudes are, however, generally considered to be H > Ph > Me, (18) to the extent that they are not competitive under similar conditions. This is also borne out in our work since the two methylidenediones which had only a phenyl or methyl group in position to migrate instead of a hydrogen atom, did not decarbonylate.



R = CH_3, Ph

In addition to this work's value as a mechanistic study, the simple procedures involved and the good to excellent yields suggests that the propargyl ester pyrolysis may be of synthetic value. The only other preparations of methylidenediones unsubstituted at the methylidene terminus which we have found are incorrect, so our reaction is, probably, the only known route to these compounds. Upon examination of molecular models, Wilson concluded that the high reactivity of the methylidenedione was due to its ability to form a planar array of both carbonyls and the olefin simultaneously. This conjugation with two carbonyls dramatically increases the olefin's susceptibility to nucleophilic addition (Michael addition). Under Knoevenagel reaction conditions, the Michael addition of a second molecule of nucleophile to the methylidenedione is too rapid to allow isolation of the methylidenedione. Adding one methyl group to the methylidene position is enough to sterically prevent conjugation of the olefin with both carbonyls, thereby, reducing its reactivity under these circumstances to that of a simple α,β-unsaturated ketone.

This reaction may also be synthetically important as a good route to open chain α,β-unsaturated ketones. α,β-Unsaturated ketones can be synthesized many ways. Some examples are: addition of vinyl Grignard reagents to anhydrides (12),

Fridel Crafts reactions (19), aldol condensations (20, 21) and the Mannich reaction (22). Industrial preparations for the lower molecular weight α,β-unsaturated ketones are also common (23-26). These generally are catalyzed oxidations or condensations.

Often these methods suffer from a lack of specificity and low yields, or involve many steps and much time. Our synthesis of vinyl ketones depends mainly on the availability of the acid, because propargyl alcohol is quite cheap and available:

$$RCO_2H + HO\text{-}CH_2\text{-}C{\equiv}CH \xrightarrow[2.\ \text{pyrolysis}]{1.\ \text{esterification}} R\text{-}CO\text{-}CH{=}CH_2 + CO$$

Other propargyl alcohols can often be prepared from various acetylenic salts and the appropriate carbonyl compounds (27).

Thus far, we have only prepared the esters <u>via</u> the acid chlorides, however, other esterification reactions are known to work for similar compounds (28) and may be preferred under certain circumstances.

A report of a radical reaction found upon pyrolysis of the propargyl ester, propargyl oxalate, has been published by Trahanovsky and Ong (6). The reason that their ester formed radicals, while our esters rearranged, is the facile cleavage of the weak central bond in the oxalate esters:

$$HC{\equiv}C\text{-}CH_2\text{-}O\text{-}CO\text{-}CO\text{-}O\text{-}CH_2\text{-}C{\equiv}CH \longrightarrow 2\ HC{\equiv}C\text{-}CH_2\text{-}O\text{-}CO^{\bullet} \longrightarrow$$

$$2\ HC{\equiv}C\text{-}CH_2^{\bullet} + 2\ CO_2 \longrightarrow PhH + 2\ CO_2$$

One must also keep in mind that pyrolyses of propargyl esters containing thermally labile substituents, such as halides, nitro groups, or other ester functions would lead to side reactions. In some cases these might be minimized by using lower pyrolysis temperatures and recycling the residual starting material.

In summary, we have studied the thermal gas phase reactions of variously substituted propargyl esters. All the esters formed one predominant product, either a methylidenedione or an α,β-unsaturated ketone. The good to excellent yields give us reason to believe the general reaction has synthetic possibilities. The mechanism favored is a series of symmetry allowed, intramolecular, concerted reactions.

EXPERIMENTAL

Common equipment

Nuclear magnetic resonance spectra (nmr) were taken on a Varian A-60 or Hitachi Perkin Elmer R-20 B. Chemical shifts are measured as values in ppm from tetramethylsilane.

Infrared spectra (ir) were obtained on a Beckman IR-12 or Perkin Elmer 21 instrument.

Gas liquid chromatography (glpc) was done on an Aerograph Model 200 instrument with dual thermal conductivity detectors.

Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected.

Pyrolysis apparatus

The pyrolysis apparatus is pictured in Figure 1. The components of the apparatus are numbered in the figure and described in the following.

1. Sample Heater. Cylindrical aluminum block, 19 cm long, 7.5 cm o.d., bored out to fit loosely over the sample holder and with a small bore through its backside into the wall to hold a thermometer, it is wrapped with heating tape and then asbestos tape.

2. Sample Holder. Made from H. V. S., ground, ₹ 40/35, O-ring joint with silicone rubber O-ring (Scientific Glass Apparatus Co., Inc.).

3. Pyrolysis Tube. Vycor glass, 12 in. long, 2.8 cm. o.d., filled with Vycor rings.

4. Furnace. 800 watt, Lindberg Hevi-Duty "Mini Mite", fitted with input controller and pyrometer (Matheson Scientific).

5. Product Trap. Joints are O-ring seal, 2.5 cm. i.d., with Buna-N rubber O-rings and appropriate clamps (Scientific Glass Apparatus Co., Inc.).

6. Stopcock. Teflon, 0-10mm (Scientific Glass Apparatus Co., Inc.).

7. Stopcock. Same as 6, 0-15mm size.

8. Line to Roughing Pump. Cenco Megavac pump (Central Scientific Co.).

9. Cold Trap.

10. Cathode Tube.

11. Cold Cathode Vacuum Gauge (H. S. Martin and Son).

12. Two Stage Oil Diffusion Pump (H. S. Martin and Son).

13. Line to Forepump. Fitted with 10 mm, glass, high vacuum stopcock and Duo Seal Model 1400 vacuum pump (Welch Scientific Co.).

Commercial materials

Common solvents and reagents were purchased from J. T. Baker Chemical Co. The sources of the other commercially available chemicals are listed in Table 7.

Figure 1. Pyrolysis apparatus

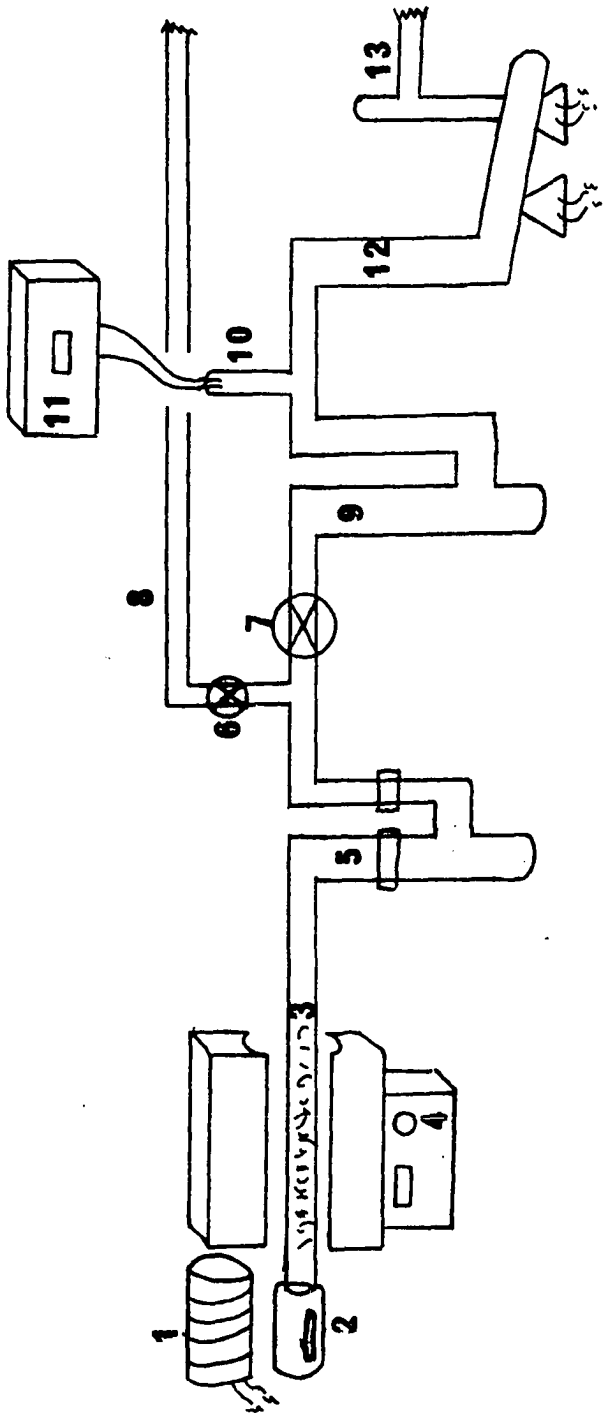

13
12
10
11
9
8
7
6
5
4
3
2
1

Table 7. Commercially available chemicals used in Part I

Compound	Source
Propargyl alcohol	Chemical Samples Co.
1-Phenylpropargyl alcohol	Chemical Samples Co.
3-Phenylpropargyl alcohol	Chemical Samples Co.
Acetyl chloride	Baker
Benzoyl chloride	Baker
Cyclohexanecarboxylic acid	Aldrich
Thionyl chloride	Fisher
Palladium on charcoal	Matheson, Coleman and Bell
Dibenzoylmethane	Aldrich
Formic Acid	Baker
Formaldehyde	Baker

Cyclohexanecarbonyl chloride

Cyclohexanecarbonyl chloride was prepared from cyclohexanecarboxylic acid and thionyl chloride by the method of Baumgarten et al. (29), bp 72°(12 torr) lit. 77° (21 torr).

Preparation of esters from acid chlorides

The esters were prepared by the dropwise addition of 0.06 mol of the respective acid chloride in 20 ml ether to a stirred mixture of 60 ml ether, 0.06 mol triethyl amine and 0.04 mol of the alcohol. The reaction was stirred at room temperature for 1 hr then poured into a separatory funnel containing 50 ml water. The organic layer was separated and washed successively with 10% hydrochloric acid, saturated sodium bicarbonate solution, and saturated sodium chloride solution. It was dried ($MgSO_4$) and distilled. A center cut of about 2 ml was taken and used for the pyrolyses. The esters were identified by nmr, boiling

Table 8a. Boiling points and nmr spectral data of propargyl esters (CCl_4)

Compound	Found bp/torr	Literature bp/torr	Resonance	Chemical Shift, δ	Pattern, Hz
$PhC{\equiv}CCH_2$-O-$COCH_3$	142°/15 [a]		CH_3	2.08	s
			CH_2	4.90	s
			Ph	7.15-7.60	m
$PhC{\equiv}CCH_2$-O-COPh	171°/1		CH_2	5.08	s
			Ph	7.10-7.55	m
			o-PhCO-	7.90-8.14	m
$PhC{\equiv}CCH_2$-O-CHO	128°/12		CH_2	4.94	d(J=0.9)
			-CHO	8.04	d(J=0.9)
			Ph	7.15-7.55	m
$HC{\equiv}CCH_2$-O-COPh	124°/12	86-87°/1 [b]	HC	2.50	t(J=2.5)
			CH_2	4.85	d(J=2.5)
			Ph	7.20-8.20	m
$HC{\equiv}CCH_2$-O-COC_6H_{11}	105°/15		HC	2.40	t(J=2.5)
			CH_2	4.61	d(J=2.5)
			C_6H_{11}	1.1-2.3	m

[a] The compound has been reported but the journal is unavailable and the abstract gives no physical constants (30).
[b] See reference (31).

Table 8a. (Continued)

Compound	Found bp/torr	Literature bp/torr	Resonance	Chemical Shift, δ	Pattern, Hz
$H_a C{\equiv}C-\overset{H_b}{\underset{Ph}{C}}-O-COCH_3$	122°/15	108°/12[c]	H_a	2.52	d(J=2.1)[d]
			H_b	6.42	d(J=2.1)
			CH_3	2.03	s
			Ph	7.20-7.60	m
$HC{\equiv}CCH_2-O-COCH_3$	121°/760	[b]			

[c] See reference (32).

[d] Very small further splitting is detectable.

point and elemental analysis, Tables 8a and 8b.

3-Phenylpropargyl-1-formate

Five grams (0.037 mol 3-phenylpropargyl alcohol and 7 g (0.23 mol) 97% formic acid were heated at 60° for 3-8 hrs. The mixture was cooled to 20°, neutralized with saturated sodium bicarbonate solution and washed with ether. The ether layer was dried ($MgSO_4$) and distilled. The product was a colorless liquid, bp 121°; nmr in Table 8a and elemental analysis Table 8b.

Hydrogenation of methylidendiones and phenyl vinyl ketone

The hydrogenation apparatus has been described by Bohlen (33). In the sample flask, 1 mmol of the compound to be reduced was added to a mixture of 10 ml ethyl acetate and 0.02 g palladium on charcoal. The compounds, 1,3-diphenyl-2-methylidene-1,3-dione, 1-phenyl-3-methyl-2-methylidene-1,3-dione and phenyl vinyl ketone, all adsorbed 1 ± 0.1 equivalent of hydrogen at atmospheric pressure. The catalyst was removed by filtration and the solvent was removed by distillation. The products were 1,1-dibenzoylethane, 1-benzoyl-1-acetylethane and propiophenone, respectively.

1,1-Dibenzoylethane: nmr (CCl_4) δ 1.43 (d, 3, CH_3, J = 7 Hz), 5.16 (q, 1, CH, J = Hz), 7.04-8.04 (m, 10, Ph).

Anal. Calculated for $C_{16}H_{14}O_2$: C, 80. 69; H, 5.89. Found: C, 80.58; H, 5.88 (Chemalytics Inc.).

1-Benzoyl-1-acetylethane: keto form, nmr (CCl_4) δ 1.39 (d, 3, CH_3CH, $\underline{J}$ = 7 Hz), 2.13 (s, 3, CH_3CO), 4.52 (q, 1, CH, $\underline{J}$ = 7 Hz), 7.20-7.59 and 7.83-8.10 (m, 5, Ph); consistent with published data (34); enol form, 1.90 (s, 3, CH_2), 2.20 (s, 3, CH_3), 7.25-7.60 (m, 5, Ph), 16.3 (s, 1, OH of enol forms).

Propiophenone: nmr ($CDCl_3$) δ 1.18 (t, 3, CH_3, $\underline{J}$ = 7 Hz), 2.92 (q, 2, CH_2, $\underline{J}$ = 7 Hz), 7.31-7.60 and 7.88 and 8.01 (m, 5, Ph); ir (neat) 1690 cm^{-1} (C=O). Both spectra were identical to those of authentic sample (Eastman).

Table 8b. Elemental analyses of phenyl propargyl esters[a]

Compound	Found		Calculated	
	C	H	C	H
$PhC{\equiv}CCH_2$-O-COPh	81.15	5.00	81.32	5.13
$HC{\equiv}CCH_2$-O-COC_6H_{11}	72.38	8.21	72.24	8.50
$PhC{\equiv}CCH_2$-O-$COCH_3$	75.75	5.72	75.83	5.80
$PhC{\equiv}CCH_2$-O-CHO	74.81	5.16	74.99	5.03

[a]Chemalytics, Inc.

1,1,3,3-Tetrabenzoylpropane

Preparation of 1,1,3,3-tetrabenzoylpropane was accomplished by two methods. The first method was that of Cannon et al. which involved the condensation of formaldehyde and dibenzoylmethane (8). These authors reported the product to be 1,1-dibenzoylethylene. The high melting point which

they reported, 177-179°, was near that which we found, 175-177°. The nmr spectrum of our product was more reasonably that of the tetrabenzoyl compound. Cannon et al. did not report nmr spectral data for their product. We also prepared the tetrabenzoylpropane via Michael addition of dibenzoylmethane to a sample of our 1,1-dibenzoylethylene from a pyrolysis of the phenylpropargyl benzoate. A mixture was made by adding 0.056 g (0.25 mmol) dibenzoylmethane and 0.059 g (0.25 mmol) 1,1-dibenzoylethylene to 1 ml ether and 1 drop diethyl amine. The reaction mixture was let stand for 1 hr at room temperature while crystals formed on the surface of the flask. The supernatant liquid was pipetted off, 0.5 ml ether was added to wash the crystals then pipetted off. The residual volatiles were removed under vacuum. The colorless crystals which we obtained by both methods had the same mp and nmr spectra. 1,1,3,3,-Tetrabenzoylpropane: nmr ($CDCl_3$) δ 5.70 (t, 2, CH_2, J = 7 Hz), 2.75 (t, 2, CH, J = 7 Hz), 7.20-8.25 (m, 20, Ph); mp 175-177°, lit (8) 177-179°.

Pyrolysis procedure

The diffusion pump was allowed to evacuate the system from the large stopcock to the pump to 10^{-6} or 10^{-7} torr while the oven and pyrolysis tube were heated. The sample, in an ignition boat, was placed in the sample holder and the system was evacuated to 0.05 torr by the roughing pump. The product trap was then cooled with liquid nitrogen, the

roughing pump sealed off and the large stopcock was slowly opened. The sample holder was heated to between 80° and 120° for less volatile compounds and sublimation of the sample usually took place over .5 to 2 hours. Upon completion, the pumps were sealed off, the trap was allowed to come to room temperature and dry air was allowed to fill the trap through the small stopcock. The trap was washed out with solvent and the products analyzed.

Analysis of propargyl cyclohexanecarboxylate products by glpc

The products of the propargyl cyclohexanecarboxylate were also washed from the trap with ether and analyzed by glpc on a 6' by ¼", 20% SE-30 on Chromosorb P column. The column temperature was 110°. A small amount of starting material was identified by peak enhancement and the only other significant peak, cyclohexyl vinyl ketone, was collected and the ketone was found to be homogeneous by nmr spectroscopy. A nmr spectrum of the crude product had indicated other products with absorptions in the same area of the spectra that the cyclohexyl protons appeared. Because nothing else was found by glpc, the other material was assumed to be polymeric. A larger scale pyrolysis (3 g) was also preformed on the cyclohexane carboxylate ester and the products were distilled. A liquid was collected, colorless, bp 75°/12 torr.

Anal. The compound was submitted twice for elemental

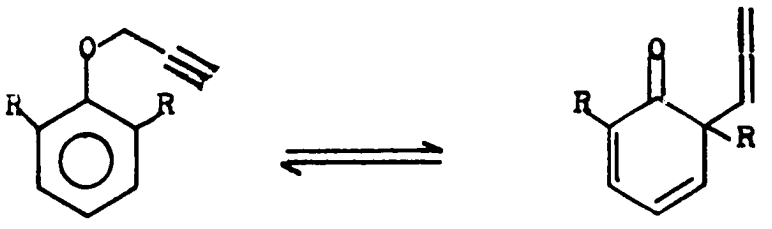
analysis but was reported to be too volatile.

The other products were analyzed only by nmr and ir spectra. The yields, pyrolyses temperatures and spectral data for all the products are summarized in Tables 1, 2, 4, 5, and 6 on pages 5, 6, 8, 9 and 10 respectively.

Part II. Gas phase thermal reactions: phenyl propargyl ethers

INTRODUCTION

Attempts to rearrange phenyl propargyl ethers (PPEs) in a manner analogous to the Claisen rearrangement of phenyl allyl ethers date back to the early part of this century (35, 36). It is only within the last few years, however, that well characterized, monomeric, rearrangement products have been isolated from liquid phase pyrolyses reactions (37, 38 and 39). In general, the first step in all the rearrangements of the PPEs appears to be the same as that of the Claisen reaction, a[3,3] sigmatropic shift;



The second step depends on the nature of the ortho substituents in the starting ether. If R = H, the intermediate tautomerizes to an allene phenol which ultimately rearranges to a benzopyran (37, 38). If R ≠ H, the intermediate cannot enolize and instead undergoes an internal Diels Alder reaction to form a metastable tricyclic ketone. The ketone ultimately rearranges to form a substituted 2-indanone (39).

In this section we will show that, in the gas phase the rearrangement of PPEs to 2-indanones is a general

reaction, regardless of the nature of the ortho substituents in the starting ether. Through the labeling of various positions on the PPEs, we are able to present a strong argument for a mechanism consisting of four thermally allowed, concerted, six electron processes. The driving force for the formation of the 2-indanone rather than the "Claisen like" product, the allene phenol, or the benzopyran product is most likely the inability of the intermediates to tautomerize in the gas phase.

LITERATURE REVIEW

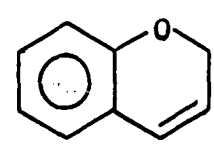
The earliest reports of phenyl propargyl ether pyrolyses are those of Powell and Adams (35) and Hurd and Cohen (36). The work of both groups was done in the liquid phase and the only products isolated were polymeric or, in some cases, monomers derived from radical reactions:

$$Ph\text{-}O\text{-}C(CH_3)_2C{\equiv}CCH_3 \longrightarrow PhOH + CH_2{=}C(CH_3)C{\equiv}CCH_3$$

For many years the consensus was that these compounds would not undergo the Claisen rearrangement reaction (40). Because of the linearity of the propargyl system, the acetylenic p orbitals are held far from the ortho aromatic carbon atom with which they must interact during a Claisen rearrangement.

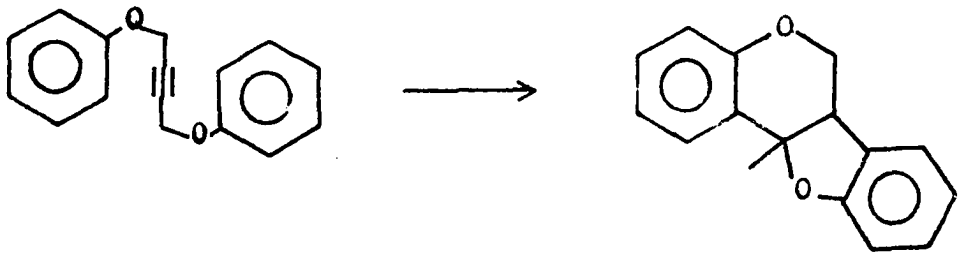
Within the last decade, however, a number of reports of thermal phenyl propargyl ether rearrangements have been published which probably involve at least a "Claisen like" [3,3] sigmatropic shift. Iwai and Ide found that by heating either phenyl or naphthyl propargyl ethers in a basic solvent for ca. 12 hr, the corresponding benzopyrans were formed in up to 90% yield (38):

$$Ph\text{-}O\text{-}CH_2C{\equiv}CH \xrightarrow[215^{\circ},\ 12\ hr]{Ph\text{-}N(Et)_2}$$

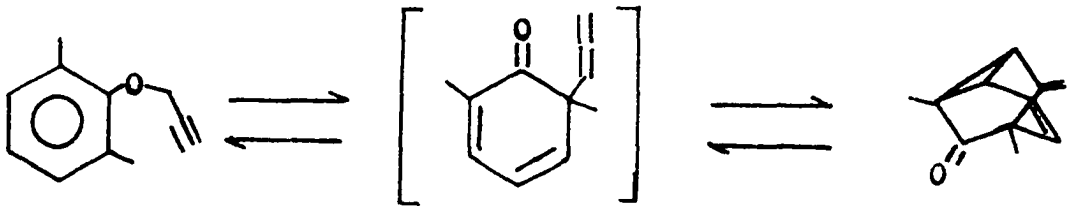


24%

Thyagarajan et al., under similar conditions, found that 1,4-diphenoxybut-2-yne rearranges to a fused ring system containing the benzopyran moity (38):



In 1968, Zsindely and Schmid reported the isolation of tricyclic ketone products upon the pyrolysis of a series of 2,6-dimethyphenyl propargyl ethers (2,6-DMPPEs) in a hydrocarbon solvent (39):



Upon further heating of the tricyclic ketone, they also found that an indanone product was formed. The indanone was later reported to be a 2-indanone, but no details were given (41).

RESULTS

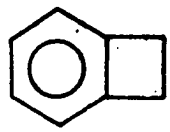
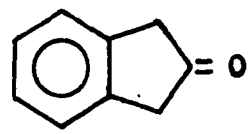
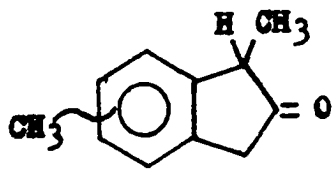
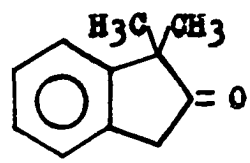
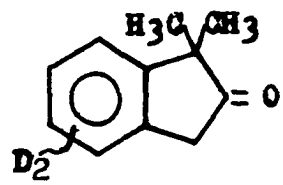
A series of phenyl propargyl ethers was prepared and subjected to gas phase pyrolysis. The products and yields are summarized in Table 9. The products were identified by their nmr and ir spectral data and by spectral and elemental analyses of their 2,4-dinitrophenylhydrazone (2,4-DNP) derivatives.

Thermal decarbonylation of 2-indanone is not known as a preparation of benzocyclobutene (42). We, therefore, questioned its intermediacy in the formation of benzocyclobutene from PPE under our conditions and pyrolyzed a sample of 2-indanone under our conditions. The 2-indanone was isolated almost quantitively. We were not able to detect any benzocyclobutene analogs in the products of our other ethers.

Two other ethers were also pyrolyzed under our conditions, phenyl γ-phenylpropargyl ether at 400° and phenyl allyl ether at ca. 500°. In both cases cleavage appeared to be the main reaction path. Only phenol was isolated from the products of the phenyl γ-phenylpropargyl ether, which was possibly formed by hydrogen atom abstraction by the phenoxide radical from the carbonaceous coating on the pyrolysis tube. Phenol, 1,5-hexadiene, and allylphenol were the main products of the phenyl allyl ether pyrolysis.

In an attempt to isolate possible intermediates, PPE

Table 9. Products and yields from gas phase pyrolyses of phenyl propargyl ethers

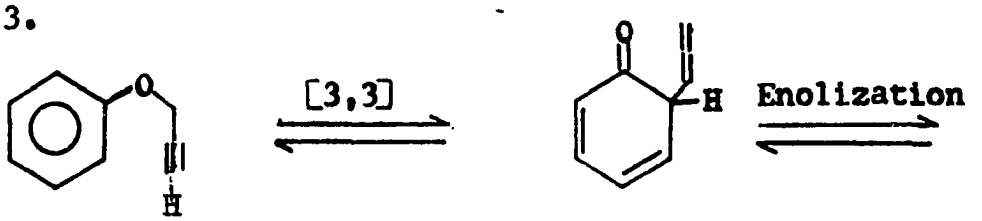
Ether	Pyrolysis Temperature	Product(s)[a] Yield, %		Starting Material, %
$Ph\text{-}O\text{-}CH_2C{\equiv}CH$ Phenyl propargyl ether (PPE)				
	400°	6	4	90
	440°	31	25	18
	460°	31	26	14
$2,6\text{-}(CH_3)_2Ph\text{-}O\text{-}CH_2C{\equiv}CH$ 2,6-Dimethylphenyl propargyl ether (2,6-DMPPE)				
	410°	65		trace
	430°	51		-
$Ph\text{-}O\text{-}C(CH_3)_2C{\equiv}CH$ Phenyl α-dimethyl-propargyl ether (α-DMPPE)				
	400°	57		trace
	400°	61		trace
$3,5\text{-}D_2Ph\text{-}O\text{-}C(CH_3)_2C{\equiv}CH$ 3,5-Dideuterophenyl α-dimethylpropargyl ether				
	400°			

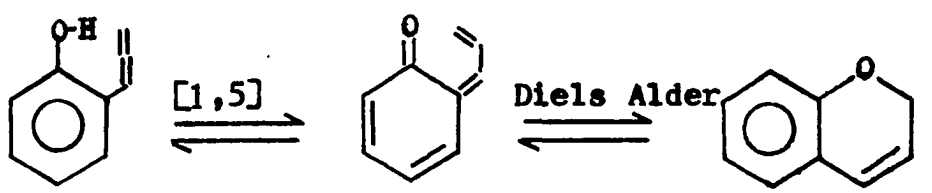
[a]Yields are absolute as determined from nmr spectrum of the product(s) with diphenylmethane or t-butylbromide as internal standard.

was also subjected to flash pyrolysis at 550° and the pyrolysate collected and analyzed on a liquid nitrogen cooled NaCl plate *via* ir spectroscopy. The outstanding feature of the ir spectrum was a 2114 cm^{-1} peak of medium intensity (the acetylenic stretch shows up at 2125 cm^{-1}) which is characteristic of a ketene absorption (43). We were unable to get a high enough concentration of the ketene compound to definitively study its thermal decay process(es). Other peaks in the ir spectrum not due to starting ester were, cm^{-1} 1756 (m), 1738 (s), 1663 (m), 1615 (s), 1486 (s). Zsindely and Schmid reported the tricyclic ketone formed from 2,6-DMPPE had ir absorptions (CCl_4) at cm^{-1} 1745, 1661, 1615, 876 (39). The similarities in the spectra suggest that we also may have isolated some of the tricyclic ketone in our flash pyrolysis work.

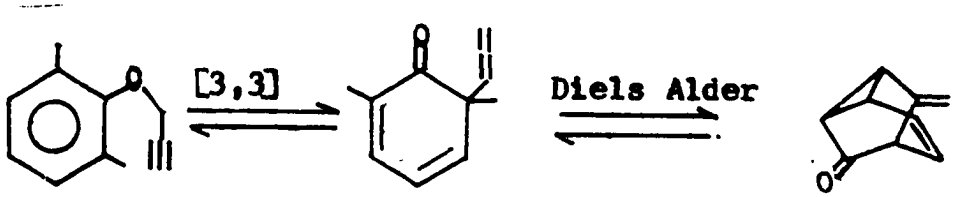
DISCUSSION

The mechanism of the liquid phase rearrangements of the PPEs has been given much attention by Zsindely and Schmid and Hansen and Schmid (39, 41). These authors explained the reactions in terms of thermally allowed concerted (with one exception, the enolization) reactions, Scheme 2 and Scheme 3.





Scheme 2. Rearrangement of phenyl propargyl ethers which do not have two ortho alkyl substituents

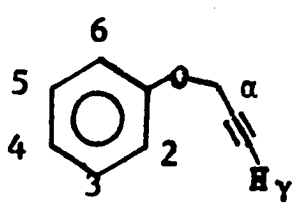


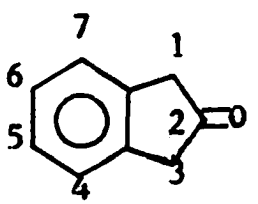
Scheme 3. Rearrangement of 2,6-dimethylphenyl propargyl ethers

These mechanisms are quite satisfactory for two reasons. First, they account for all the products reported in the rearrangement reactions. Secondly, as Schmid points out, all the steps, with the exception of the enolization, are common symmetry allowed processes. The enolization though not a symmetry allowed process is to be expected in the liquid phase because of the Claisen rearrangement analogy and is probably an ionic reaction. The inability of the 2,6-DMPPEs to enolize after the initial [3,3] sigmatropic shift, Scheme 3, is then the driving force for the tricyclic ketone formation.

We have considered two possible mechanistic pathways for the 2-indanone forming reactions in our work, Scheme 4.

In our attempts to substantiate the mechanism leading to 2-indanone formation, we have relied mainly on nmr spectral evidence because there is a large chemical shift difference between substituents on the 1 and 3 positions and those on the aromatic portion of the molecule. The following lettering and numbering system has been used throughout:

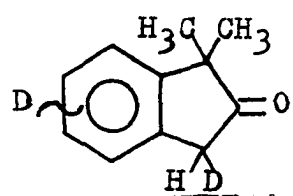




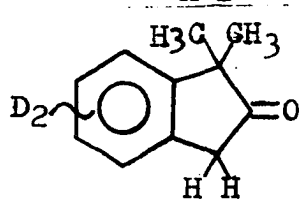
Considered first was the pyrolysis product of α-DMPPE, 1,1-dimethyl-2-indanone. This is consistent with either path 1 or 2 in Scheme 4 and pinpointed the location of the

carbon atom that was in the α position in the α-DMPPE as that carbon atom which is in the 1 position of the product. Secondly, pyrolysis of the 2,6-DMPPE gave an indanone containing one methyl in an α carbonyl position and one methyl on the aromatic portion of the molecule. This data lent credibility to the overall scheme by substantiating a mechanism in which the 2 and 6 positions of the ether had become the 3 and one of the aromatic positions of the 2-indanone product. If one knew the exact positions of the methyl groups in the product, the two mechanistic paths could have been readily distinguished. The structure might have been determined by X-ray crystallography or, perhaps, chemical means. Either method, however, would have been quite tedious.

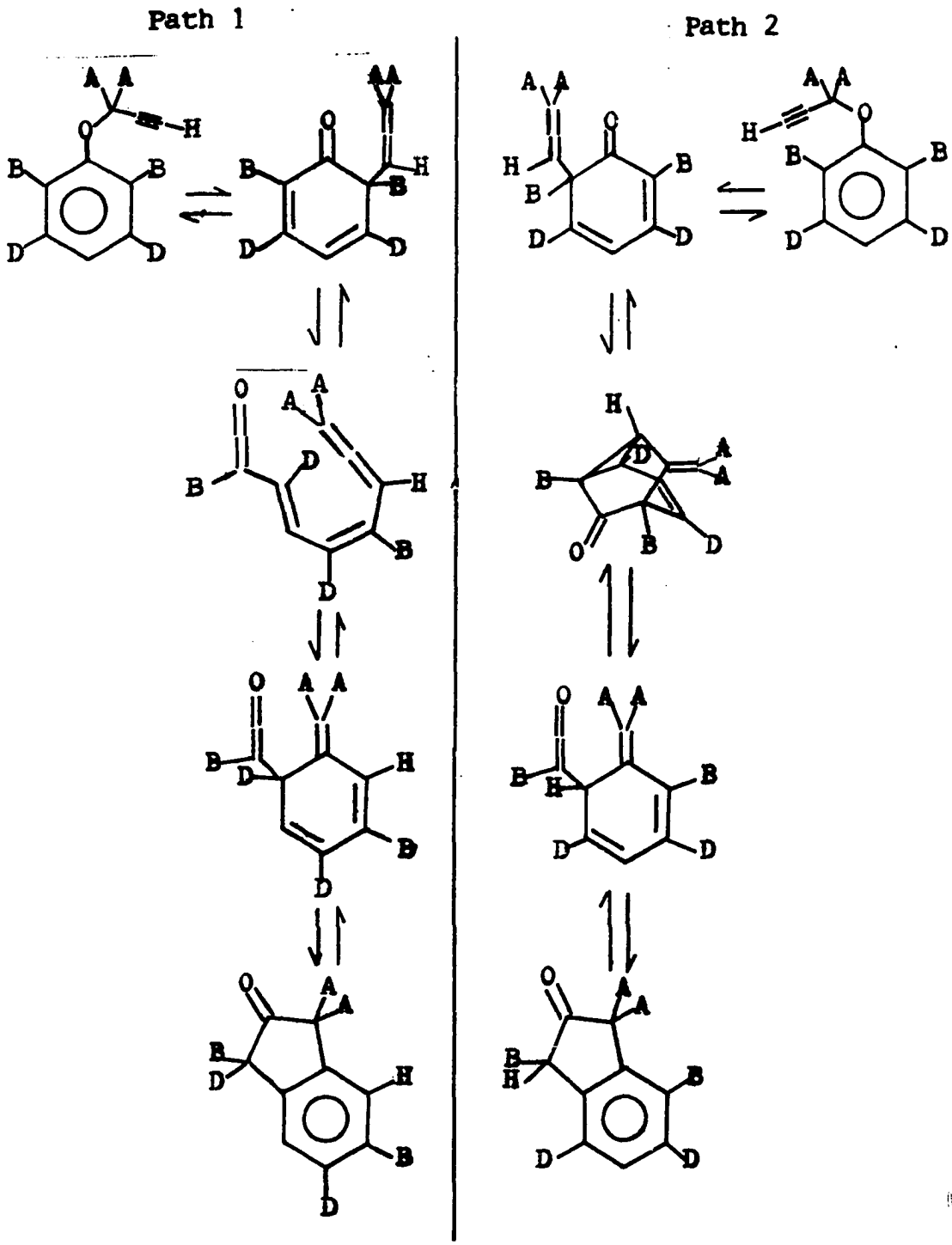
The pyrolysis product of m-dideuterophenyl α-dimethylpropargyl ether was then used to differentiate between the two paths. The two possible products are:



from path 1, and



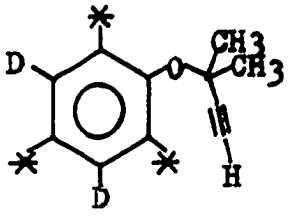
from path 2. In order to facilitate purification and handling of this 2-indanone product its 2,4-DNP derivative was prepared, recrystallyzed and analyzed for deuterium. Proof of the compound's identity was

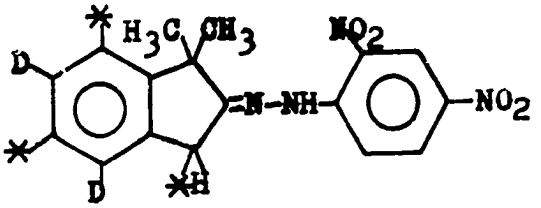


Scheme 4. Possible mechanisms for 2-indanone formation

then obtained from its nmr spectrum and elemental analysis. The ratio of the aromatic protons to proton(s) in the 3 position was ca. 1:1 as was predicted by path 2 rather than the 3:1 ratio one expected from the product of path 1. The peak in the nmr spectrum due to the methyl protons and the peaks representing the protons on the nitrated aromatic ring can be considered to be internal standards for determination of the isotopic purity of the 2-indanone.

The final steps of the reaction (path 2) were both six electron processes. The first of these was considered a reverse Diels Alder reaction to form the ketene. This is consistent with the flash pyrolysis data. The final step is then a cyclization via an "ene" or an analogous reaction with the migrating hydrogen being that which was originally in the γ position of the starting material. This was borne out by a closer inspection of the deuterium isotope content at the various positions of the starting ether and its pyrolysis product. The deuterium isotope content of the phenol used to prepare the deuterated ether was accurately determined by nmr and mass spectroscopy to be 19% deuterium isotopes in the o and p positions and ca. 100% deuterium isotopes in the m positions (see Experimental section). The actual deuterium isotopic abundances at the various positions of the deuterated propargyl ether and the 2,4-DNP derivative of the product 2-indanone are then:





* = 19% D

With the exception of the methyl groups, the terminal acetylenic position of the ether is the only position in the molecule which has 100% ^1H. Our integration of the nmr spectrum of the 2,4-DNP derivative, page 52, is consistent with the indicated isotope distribution even to the extent that the deuterium isotope abundance at position 3 of the product is 10% per hydrogen atom. That this deuterium isotope abundance of 10% is due to a 1:1 ratio of 100% ^1H atoms and 81% ^1H atoms is the most reasonable explanation for the integration and is consistent with our proposed mechanism.

We have shown then that our gas phase reactions probably parallel the liquid phase pyrolyses reactions in which enolization of the first formed intermediate is prevented by the ortho substituents. No ortho substituents are needed in the gas phase because of the inability of the

enolization reaction to occur without a catalyst (44). Also in support of this is our finding that higher temperatures are needed to decompose the phenyl allyl ether than are needed to decompose PPE under our conditions. The main product from phenyl allyl ether is probably derived from a radical reaction. It is quite possible that after the initial [3,3] sigmatropic shift the molecule finds that it is unable to enolize and therefore reverts to starting material, cleaves or rearranges to the para isomer. More work might be done in this area in the future in order to investigate these possibilities.

Other points which deserve future attention are the origin of the benzocyclobutene (BCB), and the reason that it is only formed from the unsubstituted PPE. The fact that an authentic sample of 2-indanone did not decompose when subjected to our experimental conditions would tend to rule it out as the direct precursor to the BCB. One can speculate as to other routes by which carbon monoxide may be lost. Direct decarbonylation of the ketene is a possible explanation (45). As of yet, there is not enough information available to make a reasonable guess.

EXPERIMENTAL

Equipment

The equipment, with the exception of the flash pyrolysis apparatus, has been described in Part I. The flash pyrolysis-ir spectrometer combination which we used was similar to that of King et al. (46).

Commercial materials

Common solvents and reagents were purchased from Baker Chemical Co. The other chemicals and their sources are listed in Table 10.

Table 10. Commercially available chemicals used in Part II

Compound	Source
2-Indanone	Aldrich
Propargyl chloride	Aldrich
1,5-Hexadiene	Aldrich
2-Methylbutyne-2-ol	Aldrich
2,6-Dimethylphenol	Aldrich
Phenyl allyl ether	Aldrich
γ-Phenylpropargyl alcohol	Chemical Samples
Benzene-d_6	Diaprep

α-Dimethylpropargyl chloride

2-Methyl-3-butyn-2-ol (α-dimethylpropargyl alcohol) was chlorinated with $CaCl_2$ and HCl by the method of Hennion and Nelson (47), bp 75-80°, lit. 75.5-76.5°.

γ-Phenylpropargyl bromide

γ-Phenylpropargyl alcohol was brominated by the method of Lai (48), bp 73-75°/0.05 torr, lit. 107-108°/6 torr.

3,5-Dideuteriophenol

Benzene-d_6 was converted to aniline by the method of Fieser (49). The compound was not distilled and no attempt was made to determine the deuterium content at this point. The bp of aniline was reported by Fieser as 184°.

The aniline was diazotized and hydrolyzed by the method of Ungnade and Orwoll (50). The product, a light yellow solid, was distilled, bp 180-182°; commercial sample bp 180°. The nmr of our product indicated that the ortho and para deuterium atoms had been exchanged for hydrogen atoms during the preparation; nmr (CCl_4) δ 6.72 (s, 3, o and p aromatic), 7.10 (s, 1, -OH). The hydroxy proton disappeared from the nmr spectrum upon addition of deuterium oxide to the nmr sample. According to Schug and Deck, the ortho and para protons of phenol are observed by nmr to be ca. 0.5 ppm upfield and the meta protons are ca. 0.2 ppm upfield from benzene. Because we only found aromatic protons at ca. 0.5 ppm upfield of benzene (benzene generally being 7.25-7.30), our phenol was believed to be the 3,5-dideuterated isomer (51). The facile acid catalyzed exchange of the ortho and para hydrogen atoms of phenol also indicated that only the meta deuterium atoms would remain intact after subjecting the benzene-d_6 to our

synthetic sequence (52).

Preparation of phenyl propargyl ethers

The method used was similar to that of Okajima (53). Typically, 0.1 mol of each of the appropriate phenol, propargyl chloride (or bromide) and potassium carbonate were stirred and refluxed from 6-15 hr. The mixture was then poured into 250 ml water and extracted three times with ether. The ether layer was washed three times with 10% sodium hydroxide solution and dried ($MgSO_4$). The ether was removed *via* distillation on a steam bath and the product was distilled under reduced pressure. Boiling points and melting point and nmr data are recorded in Table 11[a] except for the 3,5-dideuterophenyl α-dimethylpropargyl ether which was not distilled and used crude for pyrolysis. Elemental analyses data for some of the ethers is recorded in Table 11b. Yields were not measured because a 2-5 ml center cut was adequate for our work.

Pyrolysis procedure

The general procedure has been described in Part I. The products were washed out of the trap with an nmr solvent into a vial containing the nmr standard, diphenylmethane or *t*-butylbromide, and analyzed by nmr. The products of PPE were also washed out of the trap with benzene and the BCB separated and collected by glpc; 5'/¼" 20% SE-30 on Chromosorb P column at 90°.

Table 11a. Boiling points, melting point and nmr spectral data (CCl_4) of the phenyl propargyl ethers

Compound	bp/torr or mp	Resonance	Chemical Shift, δ	Pattern Hz
Ph-O-CH_2C≡CH	86°/15[a]	CH	2.34	t(J=2.1)
		CH_2	4.47	d(J=2.1)
		Ph	6.6-7.2	m
Ph-O-C(CH_3)$_2$C≡CH	35°/10^{-3}	CH	2.39	s
		CH_3	1.59	s
		Ph	6.7-7.3	m
2,6-(CH_3)$_2$Ph-O-CH_2C≡CH	110°/15	CH	2.29	t(J=2.5)
		CH_2	4.33	d(J=2.5)
		CH_3	2.23	s
		Ph	6.82	s(broad)
Ph-O-CH_2-C≡CPh	mp 51°[b]	CH_2	4.83	s
		Ph	6.8-7.4	m

[a]Lit. bp 96°/22 torr, see reference (52).

[b]The ether was recrystallyzed from ethanol-water. $CDCl_3$ was used as solvent for the nmr spectrum.

Table 11b. Elemental analyses of phenyl propargyl ethers[a]

Compound	Found		Calculated	
	C	H	C	H
α-DMPPE	76.89	7.00	82.47	7.54
2,6-DMPPE	82.13	7.48	82.47	7.54
γ-Phenylpropargyl phenyl ether	85.46	6.01	86.52	5.80

[a]Chemalytics Inc.

Identification of pyrolysis products

The analytical data used to identify the pyrolysis products and some of their derivatives are listed in Tables 12, 13, 14 and 15. The nmr spectra of the 2,4-DNP derivatives of 1,1-dimethyl-2-indanone and its deuterated analog are also shown in Figure 2. Phenol was the only product found in the pyrolysate of γ-phenylpropargyl phenyl ether. Phenol and 1,5-hexadiene were the only products isolated from the pyrolysate of phenyl allyl ether. Phenol and 1,5-hexadiene were identified by comparing their nmr spectra with those of commercial samples.

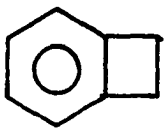
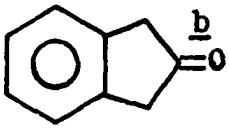
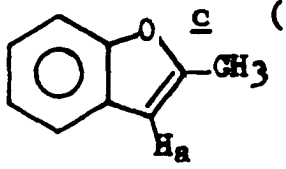
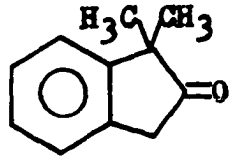
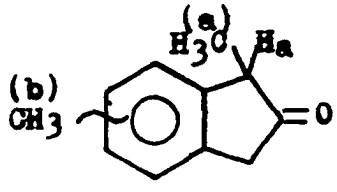
Table 12. IR spectral data of pyrolyses products from phenyl propargyl ethers

Compound	Absorption(cm^{-1})	Intensity	Phase
I[a]	2910	s	$CDCl_3$
	1450	m	
	1430	m	
	1420	m	
	1240	m	
	990	m	
II[b]	1750	s	$CDCl_3$
	1735	w	
III	1757	s	neat
IV	1760	s	neat

[a]Consistent with published spectrum (54). Structures are shown in Table 13.

[b]Consistent with published data (55).

Table 13. NMR spectral data of products from phenyl propargyl ether pyrolyses

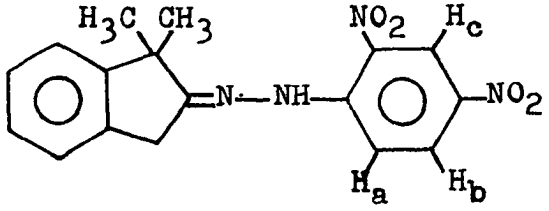
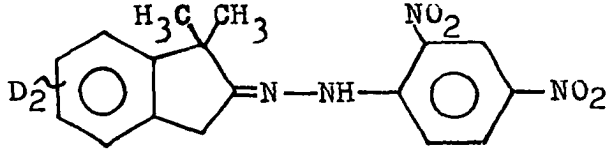
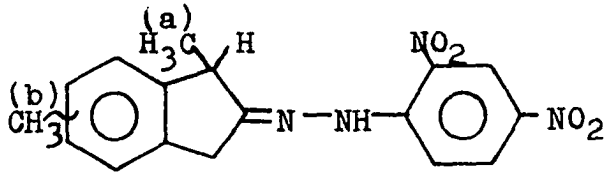
Compound	(Solvent)	Resonance	Chemical Shift, δ	Pattern, Hz
 I	($CDCl_3$)	CH_2	3.15	s
		Aromatic	6.9-7.3	m
 II	($CDCl_3$)	CH_2	3.50	s
		Aromatic	7.30	s(broad)
	($CDCl_3$)	CH_3	2.42	s(broad)
		H_a	6.20	s(broad)
 III	(CCl_4)	CH_3	1.20	s
		CH_2	3.33	s
		Aromatic	7.07	s
 IV	(CCl_4)	CH_3(a)	1.33	d(J=7)
		CH_3(b)	2.20	s
		CH_2	3.25	s
		CH	3.32	q(J=7)
		Aromatic	7.71	s(broad)

[a]Consistent with published data (56), our 2-indanone was purified only by removing the BCB under reduced pressure, further attempts to remove minor products led to decomposition.

[b]Consistent with published data (55).

[c]This (57) and styrene appeared as minor products (ca. 5%) in the pyrolysis of PPE. Similar products may be formed in the other pyrolyses, but were never identified.

Table 14. NMR spectral data of the 2,4-DNP derivatives of the substituted 2-indanones formed from pyrolyses of substituted phenyl propargyl ethers ($CDCl_3$)

Compound	Resonance	Chemical Shift, δ	Pattern, Hz
	CH_3	1.51	s
	CH_2	3.87	s
	Aromatic	7.25	s(broad)
	H_a[a]	7.95	d(J=9)
	H_b[a]	8.25	d of d(J=9) (J=2)
	H_c[a]	9.07	d(J=2)
	NH[a]	11.0	s(broad)
	CH_3	1.50	s
	CH_2	3.87	s
	aromatic	7.25	s(broad)
	CH_3(a)	1.53	d(J=7)
	CH_3(b)	2.34	s
	CH	3.86	q(J=7)
	CH_2	3.69	s(broad)
	Aromatic	7.12	s(broad)

[a]This portion of spectra was same for all samples.

Table 15. Melting point and elemental analysis data of 2,4-DNP derivatives

Compound	mp	Calculated,			Found[a]		
		C	H	N	C	H	N
V	190-191°	60.00	4.71	16.50	59.99	4.73	16.63
VI	187-188°						
VII	202-203°	60.00	4.71	16.50	59.99	5.04	16.55

[a]Chemalytics Inc.

Analysis of the deuterium content in the deuterated phenol, anisole and 2-indanone

The deuterated phenol was analyzed by nmr, (CCl_4) δ 6.74 (broad s, 145 integral units), 7.08 (s, 55 integral units). The low field peak, OH, disappeared upon shaking the sample with deuterium oxide. No meta hydrogen signal was observed (56). By comparing the integrals of the hydroxy proton and the ortho and para protons one finds ca. 13% deuterium atoms in the ortho and para positions.

The deuterated anisole derived from the phenol was analyzed by nmr and mass spectroscopy. NMR, (CCl_4) δ 6.77 (broad s, 39 integral units/H), 3.50 (s, 46 integral units/H). This indicates ca. 15% deuterium atoms in the ortho and para positions by comparing the integral of the methyl protons' signal with that of the aromatic region. The mass spectral data for the deuterium analysis is summarized in Table 16. Because the nmr spectrum indicated that the meta positions were completely deuterated, we calculated the ortho and para deute-

rium isotope content in the following manner. All the $\underline{d}_1$ and $\underline{d}_2$ were considered to be meta. One third of the $\underline{d}_3$ and two thirds of the $\underline{d}_4$ were then considered to be in each of the three remaining positions. Therefore, the total deuterium isotope content, for these positions is:

$$41\%/3 + 8\%/1.5 = 19\%$$

Table 16. Mass spectral data for natural and deuterated anisole

m/e	Deuterium content	Intensity of natural sample[a]	Intensity of deuterated sample[b]	Corrected intensities
108	$\underline{d}_0$	100	-	-
109	$\underline{d}_1$	8.3	2	2
110	$\underline{d}_2$	0.9	44	44
111	$\underline{d}_3$	-	42	38(41%)
112	$\underline{d}_4$	-	10	7(8%)
113	$\underline{d}_5$	-	2	1

[a]Average of three determinations at 14 and 16 ev.

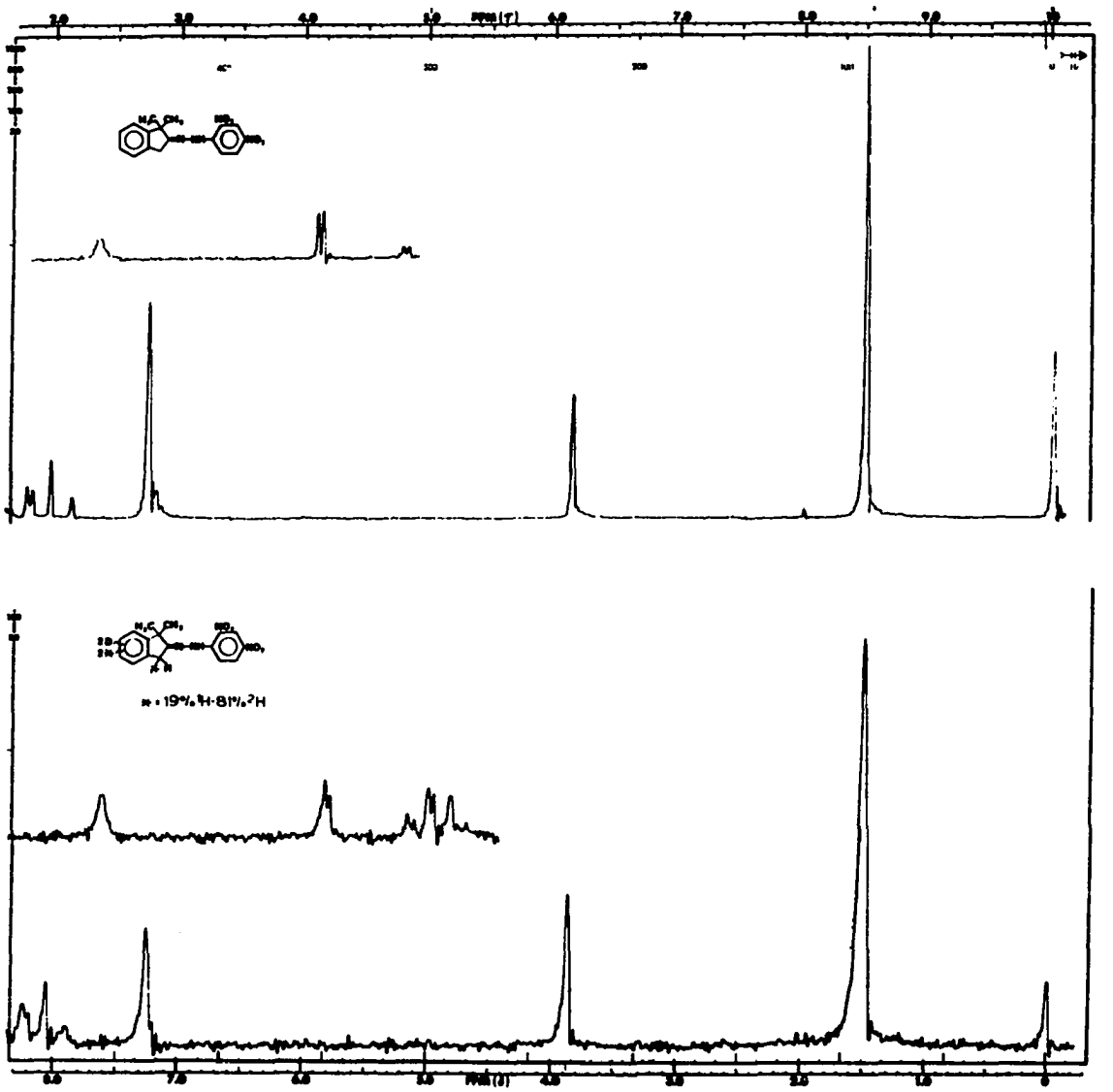
[b]Average of four determinations at 70, 20 and 13 ev.

The deuterated indanone product was first converted to a 2,4-DNP derivative and then analyzed for deuterium content by its nmr spectrum, Figure 2. The chemical shifts are also summarized in Table 14. The protons signals of the 2,4-dinitro aromatic ring and those on the methyl groups integrated at 35 integral units/H.

The proton signal from the 3 position totaled 64 integral units or 32/H. According to the mechanism, one of these protons is derived from the ortho position and should be ca. 20% deuterium isotope; and the other is derived from the γ position of the ether and should be 100% ^{1}H. The integration of 32/H is consistent with the predicted average of 10% deuterium isotope abundance at this position.

The aromatic proton signal of the indanone integrates at a total of 58 units. Because two of the four positions are 100% deuterium atoms the remaining two positions have an area of 29 integral units/H. This is ca. 20% lower than the integrations of the positions which are 100% ^{1}H and is consistent with the mechanism and the deuterium isotope abundance analyses of its precursor.

Figure 2. NMR spectra of the 2,4-DNP derivatives of natural and deuterated 1,1-dimethyl-2-indanone. The upper portion of each spectrum is offset 200 Hz.



Part III. Gas phase thermal reactions: cinnamyl derivatives

INTRODUCTION

Free radical cyclization reactions are common in organic chemistry nevertheless, the effects of substituents on these reactions have not been studied extensively (58, 59, 60, 61). Many difficulties are associated with the gathering of data relating to substituent effects. The radical is a neutral species (neutral carbon radicals are the only type being considered) and does not experience the large electronic forces that charged molecules do. The rate determining step in these reactions is often the radical formation step which allows the intermediate little opportunity to exercise discretion in its subsequent reactions (59). Two other common complicating factors are chain reactions (58) and surface effects (62).

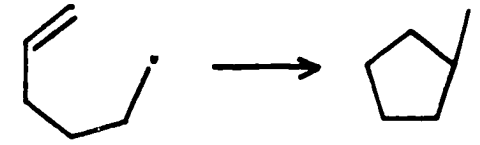
Two groups have recently reported finding kinetic isotope effects in radical cyclization reactions (6, 61). This indicated that the rate determining steps in their reactions involve cleavage of a C-H or a C-D bond at the position which had been enriched in deuterium atom abundance. Of these reactions, we believe the cinnamyl radical cyclization reaction of Trahanovsky and Ong is the best system for substituent effect studies (6). It has the highest deuterium isotope effect, $k_H/k_D = 2.92$, and is more simple because it is a gas phase reaction.

Three cinnamyl radicals were studied by us, the <u>ortho</u>-

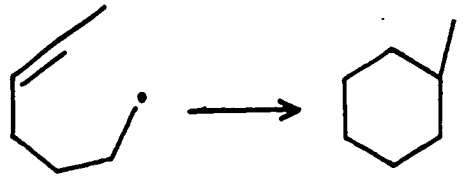
methyl, ortho-trifluoromethyl and ortho-ethyl. The first two differed only in their electronic nature and not sterically. The product ratios, (indene/substituted indene), derived from the first two radicals were shown to be 2 and ~0.008 for the methyl and trifluoromethyl case respectively. An attempt to extend this work to the ortho-ethyl cinnamyl radical resulted in a (indene/substituted indene) ratio which varied from ca. 0.1 to 0.6. The predominant products of the reaction, however, were naphthalene derivatives. We believe that the latter (indene/substituted indene) product ratio does not adequately reflect the true nature of the reaction.

LITERATURE REVIEW

Julia's recent review, probably the most extensive compilation of radical cyclization data, explores the role of many factors involved in radical cyclization reactions (58). While convincing evidence is presented to demonstrate a definite steric effect in the cyclization step of variously substituted 5-hexenyl radicals during the formation of cyclohexane or cyclopentane derivatives,



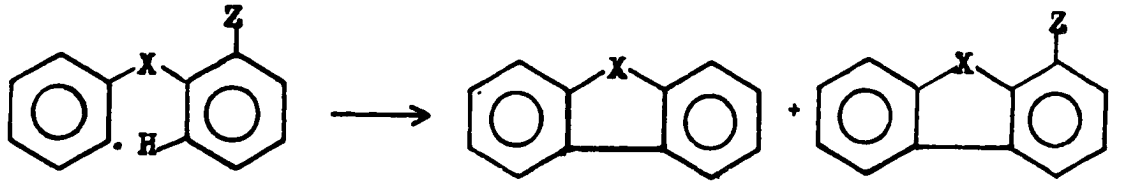
Major product



Major product

The author readily admits that other factors are involved, such as the nature of the initiator and solvent and the stability of the open-chain hexenyl radical.

The Pschorr reaction, while not always accepted as a radical reaction, has been studied a great deal for the purpose of determining substituent effects on the reaction. In these particular Pschoor reactions,

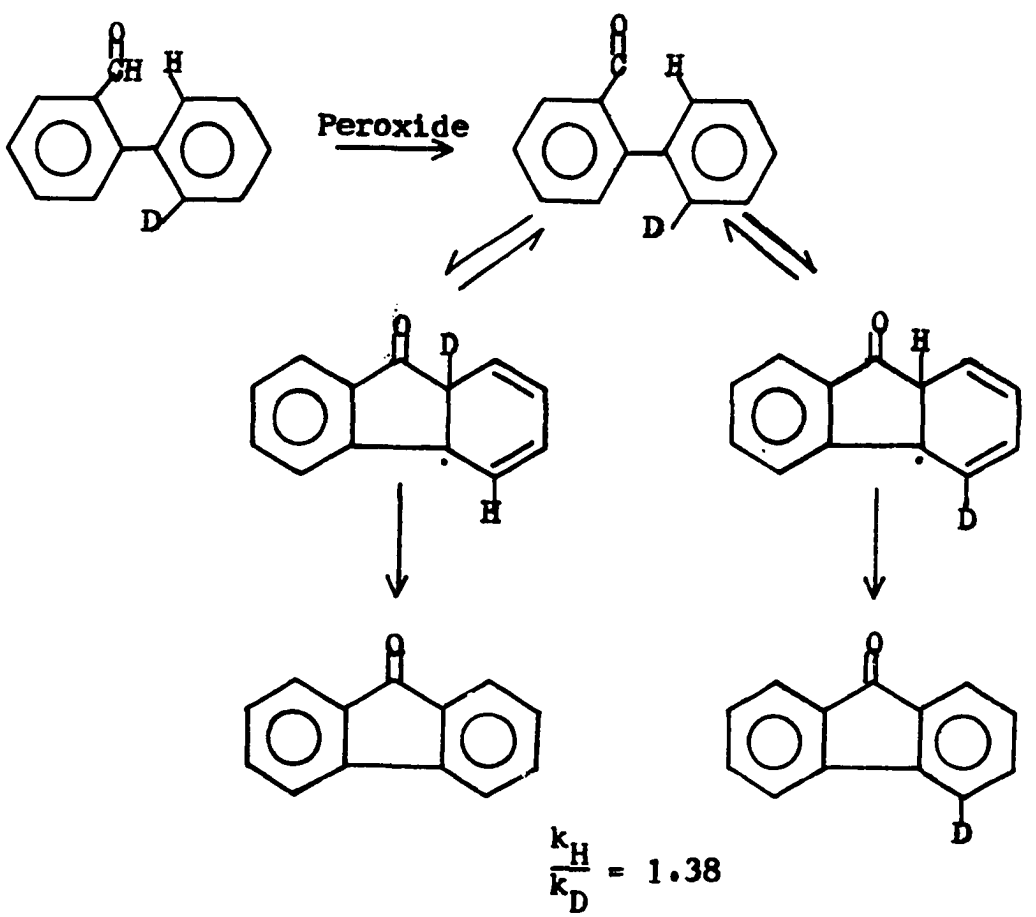


I II III

Z = NO_2, CH_3, OCH_3, CO_2H

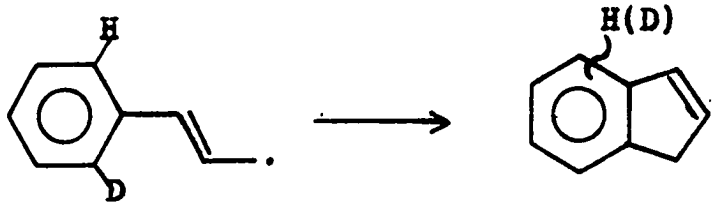
only in the case where Z = NO_2 does the formation of II compete with formation of III. Rate data for these and similar reactions cannot be determined directly because formation of I is the slow step.

In 1958, Denney and Klemchuk reported finding a deuterium isotope effect in the cyclization of the o-phenylbenzoyl radical. Mechanistically, this effect was interpreted as being due to a competitive loss of hydrogen and deuterium atoms in the rate determining step of the reaction (61). This also implies that the radical cyclization step is reversible:



$$\frac{k_H}{k_D} = 1.38$$

Gas phase pyrolysis of di-trans-o-cinnamyl oxalate has been shown recently by Trahanovsky and Ong to display an even greater isotope effect (6):



$$\frac{k_H}{k_D} = 2.92$$

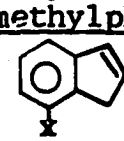
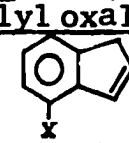
Again the effect is best explained in terms of a reversible radical cyclization step with a slow loss of either a hydrogen or deuterium atom. The simplicity of their system, there are no solvents or catalysts to contend with, and the high isotope effect which has been found for this reaction has prompted our study.

RESULTS

Pyrolysis of the di-o-methylcinnamyl (OMC) and di-o-trifluoromethylphenylallyl (OTMP) oxalate (63)

The oxalate diesters were pyrolyzed at 570-590° in our flow system. The products and yields are summarized in Table 17.

Table 17. Products and yields from pyrolyses of di-o-methylcinnamyl and di-o-trifluoromethylphenylallyl oxalates

Oxalate	Pyrolysis temperature	Indene Yield, %	 Yield, %	
di-OMC[a]	590°	31%[b]	I----18%[c]-----I	
	580°	22%	I----11%------I	
	570°	23%	I----12%------I	
di-OTMP	570°	0.5%[d,e]	24%	30%
	570°	---	27%	33%
	570°	---	27%	35%

[a] 10% 1,2-Dihydronaphthalene was also found as an OMC oxalate product.

[b] All yields shown are absolute as determined by glpc with an internal standard, mesitylene or biphenyl.

[c] The substituted indenes were collected with the 1,2-dihydronaphthalene from the glpc and their yields calculated from an nmr spectrum of the mixture.

[d] Indene was not detected as a product. The number shown is the lower limit of our ability to identify indene.

[e] NMR spectral analyses of the OTMP ester products using an internal standard, methyl isobutyl ketone, were consistent with the glpc data.

Indene was identified by comparison of its nmr and mass spectra with the spectra of a commercial sample. 1,2-Dihydronaphthalene was identified by comparison of its glpc retention time and nmr spectrum with the retention time and nmr spectrum of a commercial sample. The unseparated isomeric methylindenes were collected by glpc and their nmr spectra were found to be consistent with published data (64). The two tri-fluoromethylindenes were collected separately by glpc and identified by ^{1}H and ^{19}F nmr and mass spectroscopy. Minor constituents (0-4%) noted in the product nmr spectra were, OMC ester and alcohol, the rearranged di-o-trifluoromethylcinnamyl oxalate and corresponding alcohol, and some of the β-methylstyrenes. These minor products were identified only by nmr spectroscopy. Similar minor products were found in the pyrolysate of the unsubstituted dicinnamyl oxalate (6).

Pyrolysis of di-o-ethylcinnamyl oxalate, o-ethylcinnamyl formate and o-ethylphenylallyl acetate

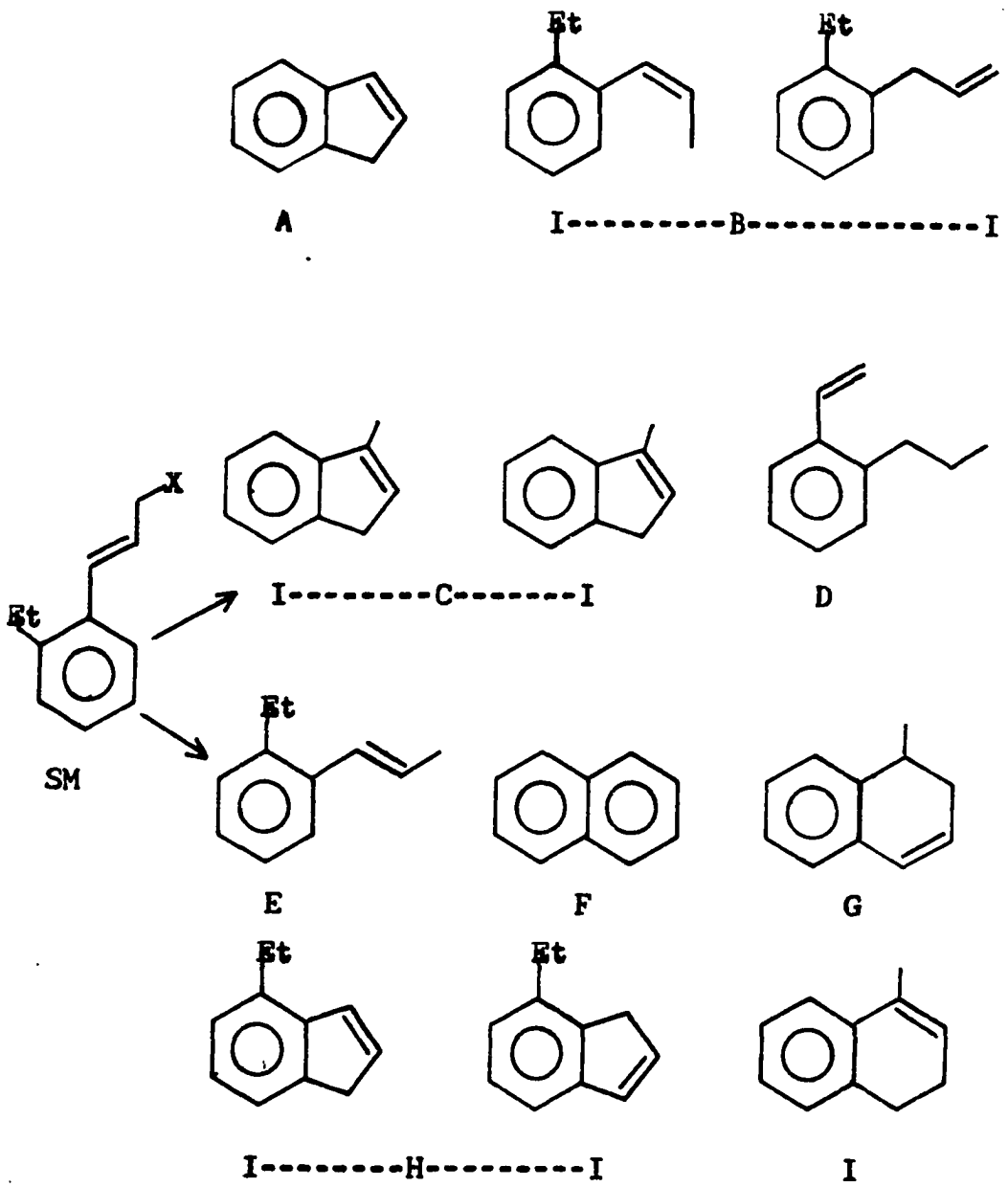
The di-o-ethylcinnamyl (OEC) oxalate was pyrolyzed as before, the ester's low volatility, however, necessitated heating the sample holder to ca. 200° in order to achieve an appreciable rate of vaporization. At this temperature most of the compound decomposed in the sample holder to form non-volatile products. The total overall yield of the products from the gas-phase reaction was only ca. 30%. The purity

of the oxalate was no more than 85%, so data from this pyrolysis reaction was too questionable to use.

Other OEC derivatives, the formate and chloride, and o-ethylphenylallyl acetate were then used as the OEC radical precursors for our work. Gas-phase pyrolyses of both the unsubstituted cinnamyl acetate and formate have both been shown to produce indene in amounts comparable to those formed via pyrolysis of the unsubstituted di-cinnamyl oxalate (6). Gas phase pyrolyses of tertiary organic chlorides has been demonstrated to produce radicals via homolytic cleavage of the C-Cl bonds (65). Because the cinnamyl radical is of comparable stability to a tertiary radical, we assumed that it would also be formed from the chloride under our conditions.

The products of the reactions are shown in Scheme 5. The yields are summarized in Table 18. Indene and naphthalene were identified by their glpc retention times and their nmr spectral data. Both the retention times and nmr spectra were found to be identical to those of commercial samples of the corresponding compounds. The remaining products were identified by individual collection of the substance accounting for a particular glpc peak and subsequent analyses of its nmr spectra. While nmr spectra of these compounds were not available for comparison, spectra of similarly substituted compounds were and assignments were mainly based on data from them. Because the glpc retention times of all the products

were between the retention times of indene and 1-methylnaphthalene on an SE-30 glpc column, it was also reasonable to expect that the molecular weights of the products were similar to those of indene and 1-methylnaphthalene. This is also consistent with the product assignments we made.



Scheme 5. Products of the pyrolyses of the o-ethylcinnamyl formate and chloride, and o-ethylphenylallyl acetate

Table 18. Yields from pyrolyses of o-ethylcinnamyl or o-ethylphenylallyl compounds

S. M. (Pyrolysis temperature)	Total Abs Yield[a,b], %	A	B	C	D	E	F	G	H	I
Acetate	66	5.5	?[c]	19.1	10.0	?	24.7	20.1	7.6	13.3
(680°)	66	4.9	?	20.3	10.8	?	22.3	21.5	8.6	11.5
Formate	74	4.5	26.5	I--17.3--I		22.0	3	13.2	10.6	trace
(640-650°)	62	4.2	26.2	I--20.1--I		27.0	3	13.0	9.4	trace
	64	4.3	26.2	I--19.1--I		26.0	3	13.7	10.5	trace
Chloride	55	2.2	?	10.3	7.3	?	5.1	43.7	31.4	2-3
(620°)	75	2.0	?	10.2	5.2	?	9.3	63.5	10.0	2-3
	57	1.0	?	5.3	6.1	?	9.1	57.5	20.9	2-3

[a]Yields were determined by glpc with an internal standard.

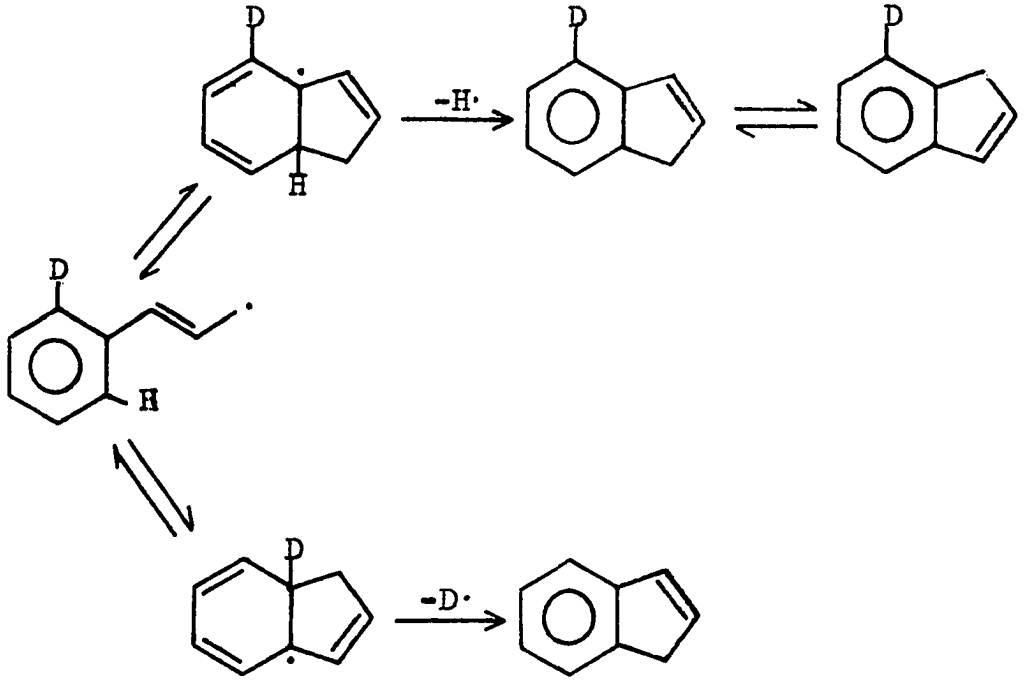
[b]All other yields are relative. A small peak at the retention time of 1-methylnaphthalene was also noted, but was too small to collect.

[c]Where a ? is placed trace amount peaks were noted at the retention time, but were too small to identify.

DISCUSSION

Pyrolyses of the di-o-methylcinnamyl and di-o-trifluoromethylphenylallyl oxalates

The reaction mechanism postulated by Trahanovsky and Ong is quite reasonable in view of the large deuterium isotope effect found, $k_H/k_D = 2.92$ (6).



Our work was an attempt to detect the sensitivity of the reaction to other substituents which varied only by their electronic nature. Because of the similarity of the radii associated with the methyl and trifluoromethyl groups and the large electronic differences associated with the hydrogen and fluorine atoms, we considered the methyl-trifluoro-

methyl comparison to be particularily good for our work. Extension of the radical cyclization work to the methyl and trifluoromethyl substituted radicals is also particularly interesting because these substituents are not usually considered as potential leaving groups in homolytic aromatic substitution reactions (66, 67, 68).

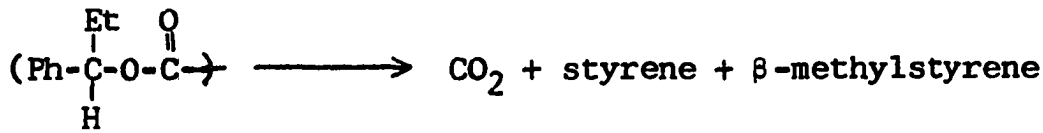
The two product ratios found, (indene/methylindene) = 2 and (indene/trifluoromethylindene) $\leq$ 0.008, indicated that displacement of the methyl group does indeed compete with displacement of a hydrogen atom (the anomalous product, 1,2-dihydronaphthalene, will be discussed with the CEC radical work). The reason for the competitive loss of methyl radicals ($CH_3^{\bullet}$) and hydrogen atoms ($H^{\bullet}$) in our work is not entirely clear. Hydrogen atoms are generally believed to be abstracted by other radicals in the product forming step of the aromatic substitution reactions. In reactions in which $CH_3^{\bullet}$ have been lost from the intermediates, the mechanism is generally believed to involve an ejection process (67).

We have considered three different mechanistic combinations of product forming steps which might account for our data. First, both the $CH_3^{\bullet}$ and H° are abstracted by other radicals. Second, the $CH_3^{\bullet}$ are simply ejected and the $H^{\bullet}$ are abstracted. Third, both species are ejected.

Radical stabilities do appear to play an important role in the rate of the product forming step. The trifluoromethyl

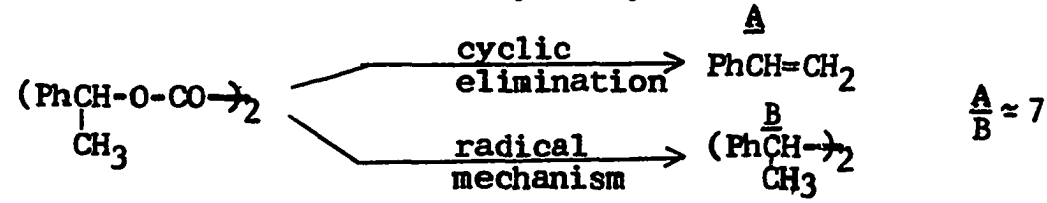
radical is generally accepted to be less stable than the methyl radical because of relative formation and hydrogen abstraction rates (67, 68, 69, 70). The different (indene/substituted indene) ratios found in this study were certainly due, at least in part, to the stability of the leaving radical.

In a related study, the pyrolysis of di-α-ethylbenzyl oxalate, Trahanovsky *et al.* reported finding a (styrene/methylstyrene) product ratio of 0.43/1 (71):



Their product ratio is nearly the inverse of that found in our work. It showed, nevertheless, that a large amount of styrene is formed despite competition from the concerted cyclic elimination of an acid molecule in the methylstyrene formation. The concerted elimination is a general pyrolysis reaction of esters which contain hydrogen atoms β to the ester.

Qualitatively, one can say that the cyclic elimination reaction is faster than α-ethylbenzyl radical formation by considering the product ratio found by Trahanovsky *et al.* upon pyrolysis of the di-α-methylbenzyl oxalate (71):



The possibility of H$^{\bullet}$ being ejected is also worth consideration. Some examples of similar processes have been reported (72, 73). Pryor and Henderson have detected the formation of hydrogen molecules during a liquid-phase reaction (72). Apparently this was a result of homolytic cleavage of S-H bonds and subsequent coupling of the hydrogen atoms which had been formed. An example more relevant to our work is that of Szwarc and Roberts (73). They found that toluene and substituted toluenes formed benzyl radicals upon pyrolysis at ca. 1000^{o} in the gas phase. These pyrolyses must involve ejection of H$^{\bullet}$ via homolytic C-H bond cleavage. In our work there is an additional driving force for the loss of H$^{\bullet}$ because the products of this process are aromatic:

In conclusion, the cinnamyl radical cyclization reaction was shown to be very sensitive to the electronic nature of the ortho substituent. That the cyclization step is reversible has previously been demonstrated by a deuterium isotope effect study. The relative rates of the slow step of the reaction, loss of the ortho substituent or a hydrogen atom, depend somewhat on the stability of the radical form of the ortho substituent. The true natures of the processes by which the H$^{\bullet}$ and the methyl or trifluoromethyl substituents are lost in the reaction are not known at this time.

Ortho-ethylcinnamyl radical precursors

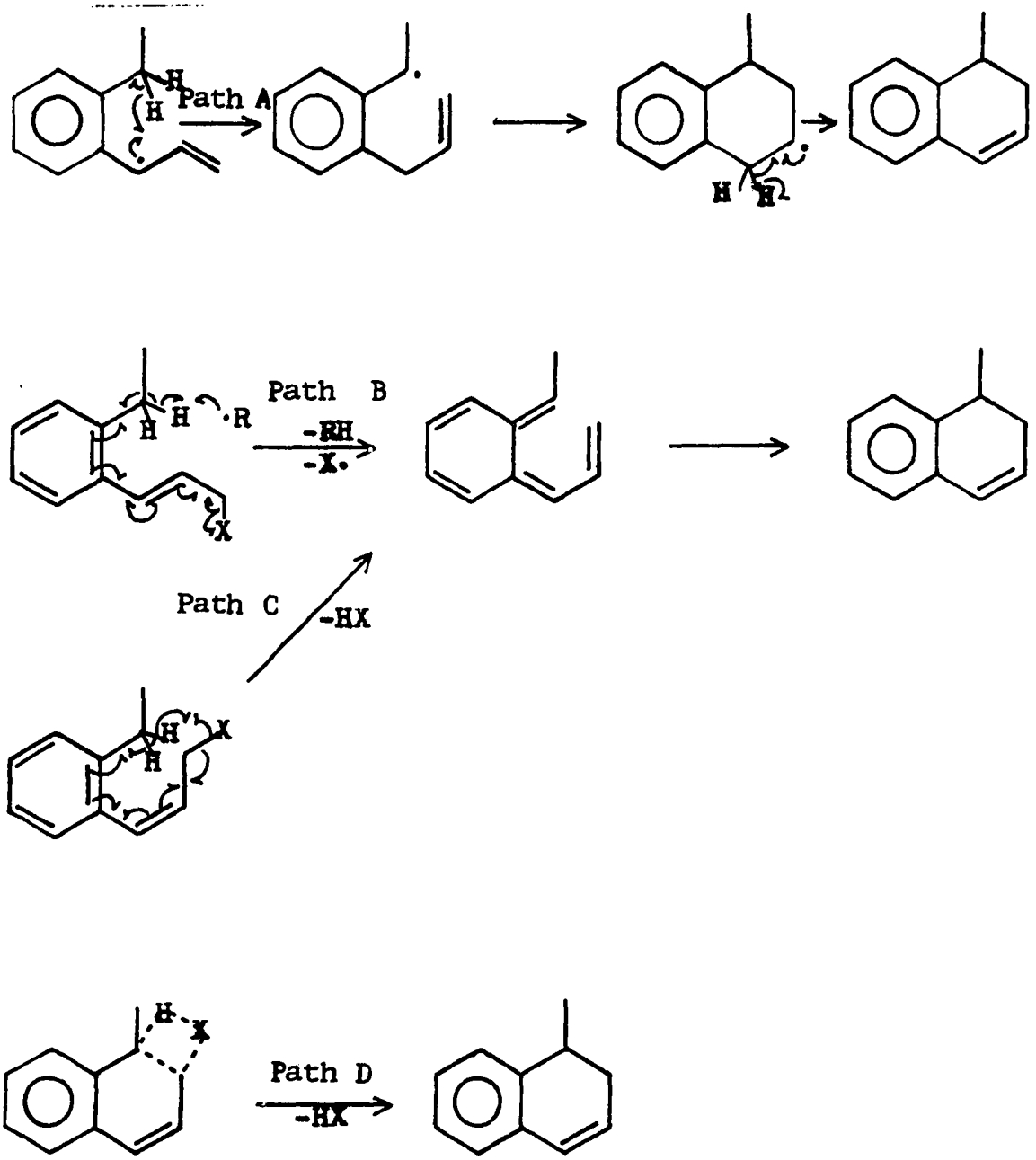
Considering the results we had obtained from the ortho-methylcinnamyl radical, one would have expected that the major products of the ortho-ethylcinnamyl (OEC) radical would have been indene, ethylindenes and methyldihydronaphthalenes. Inspection of the glpc trace of the di-OEC oxalate products showed that at least ten significant products were present. The low overall recovery, ca. 30%, and purity of the oxalate, ca. 80%, led us to consider other precursors for the OEC radical. Trahanovsky and Ong had reported that pyrolyses of cinnamyl formate and acetate at 650° had given 0.82 mol and 0.72 mol of indene, respectively, these yields were similar to those found for the oxalate (6). The chloride derivative was also considered as a radical source because chlorides which can form stable radicals are known to cleave homolytically in the gas-phase (65).

The glpc traces of the products from the pyrolyses of all the compounds were quite complex but similar. The main exceptions to this were peaks later identified as being due to o-ethylallylbenzene and its isomeric cis- and trans-β-methylstyrenes in the product glpc of the formate ester reaction. Pyrolysis of trans-cinnamyl formate at 332-342° in a static system has been reported to form allylbenzene and carbon dioxide, probably by a concerted transfer of the formate hydrogen atom to the benzilic position of the molecule as

the carbon dioxide is formed (74). While the unsubstituted cinnamyl formate gave only indene at higher temperatures, like ours, steric interference of the o-ethyl group may have retarded formation of the o-ethylcinnamyl radical by forcing the allyl portion of the molecule out of the plane of the benzene ring; thus inhibiting resonance stabilization of the incipient radical by the phenyl portion of the molecule.

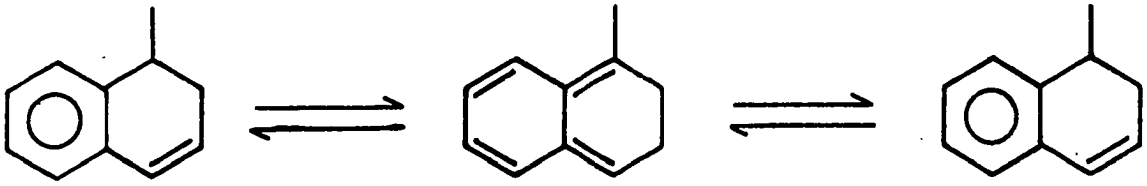
The other products, mainly naphthalene derivatives, are likely to be due to facile hydrogen atom abstractions from the benzylic position of the ethyl group. The rate of benzilic hydrogen abstraction from ethylbenzene is known to be much faster than the corresponding abstraction from toluene (67). This facile abstraction process is reflected in a number of mechanistic pathways to the dihydronaphthalene shown as Scheme 6. Path C is the intramolecular analog of Path B. Path D is just another way of looking at C and is similar to the transition state proposed for the loss of HCl from cyclohexyl chloride (75) or o-methylbenzyl chloride (76). It is possible that there is competition between the different paths and that the relative contributions of each vary with the particular starting material. The same mechanism(s) can be proposed for the formation of 1,2-dihydronaphthalene from the OMC radical.

Formation of the 1-methyl-1,2-dihydronaphthalene from the 4-methyl compound is a reaction which is analogous to the

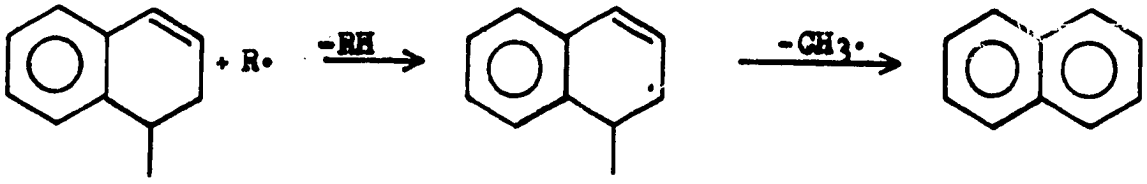


Scheme 6. Possible mechanistic pathways for formation of a dihydronaphthalene derivative from the o-ethylcinnamyl radical

indene isomerization reported by Miller and Boyer (18):



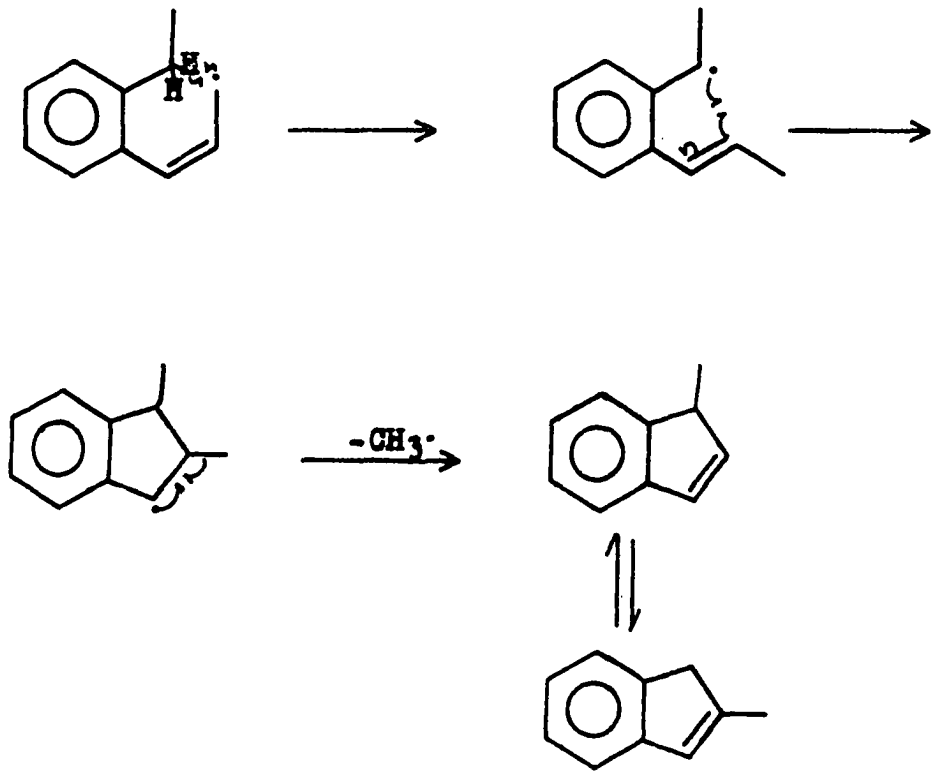
Loss of methane from 1-methyl-1,2-dihydronaphthalene is possibly an explanation for the formation of naphthalene:



It is quite likely that other unknown factors are involved in this reaction. In none of our reactions was a significant amount of 1-methylnaphthalene found despite the high probability that the benzilic hydrogen atom which is a to the methyl group would have been rapidly abstracted.

The formation of naphthalene <u>via</u> static pyrolysis of 2- and 3-methylindene over palladium and charcoal at 450° has been reported by Ruzicka and Peyer (77). Though their conditions were quite different from ours, we believe that there is a remote possibility that this reaction occurs in our work.

The origins of 2- and 3-methylindenes themselves are obscure. Indirect formation of these isomers from 1-methylindene is possible:



Thermal equilibration of 1-methylindene is expected to yield 3-methylindene and, perhaps, a small amount of the 2-methylindene (18). The nmr spectrum of our mixture of the 2- and 3-methyl isomers showed that the 3-methyl isomer predominated, but there was also a substantial amount of the 2-methyl isomer. This unexpected product ratio may simply indicate that our product ratio is kinetically controlled.

The final product to be considered, o-propylstyrene, is also the most unexpected, because it is the only cinnamyl radical product ever found by us which contained a saturated propyl side chain. This product is interesting because one

might postulate that it was formed *via* absorption of atomic hydrogen. A point relevant to the previous discussion concerning possible $H^{\bullet}$ ejections from intermediate radicals. Isomerization of *o*-ethyl-β-methylstyrene, a product of a hydrogen atom abstraction by the corresponding cinnamyl radical, however, might also account for this product (18).

In conclusion, we have found product ratios of (indene/ethylindenes) which varied from *ca.* 0.1 to *ca.* 0.6 upon the pyrolyses of *o*-ethylcinnamyl formate and chloride and *o*-ethylphenylallyl acetate. In no case, however, did the indene forming reactions compete favorably with the formation of a number of naphthalene derivatives and the ratio obtained is probably meaningless as a substituent effect study, which was our original purpose. The other reactions are interesting in themselves in that they provide a qualitative view of the cinnamyl radical's behavior when placed in the vicinity of an easily abstracted benzylic hydrogen atom. The large number of products formed attest to the complexity of the reactions involved.

EXPERIMENTAL

Equipment

The equipment used and the pyrolysis technique have been described in Part I. Elemental analyses were done by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Preparation of o-methyl-, o-trifluoromethyl-, and o-ethylphenylpropen-1-ol

The alcohols were prepared from the corresponding ortho substituted bromobenzenes by the method which Ouellette et al. had used to prepare similar alcohols (78). The o-ethyl alcohol could be rearranged to the cinnamyl alcohol by the method of Pocker and Hill (79), or could be directly converted to the ester. No attempt was made to rearrange the o-methyl alcohol. The o-trifluoromethyl alcohol resisted the acid catalyzed rearrangement so it was converted directly to the oxalate after it was distilled (o-trifluoromethylpropen-1-ol, bp $64^{\circ}/0.3$ torr). The other alcohols were used without purification.

Preparation of oxalate esters

The oxalate esters were prepared by the method of Trahanovsky et al. (71). The nmr spectral data for the esters is reported in Tables 20 and 21.

Di-o-methylphenylallyl oxalate was rearranged to di-o-methylcinnamyl oxalate by heating it at 200° for 10-15 min. It was then recrystallyzed from 95% ethanol, mp $88\text{-}89^{\circ}$.

Anal. Calculated for $C_{22}H_{22}O_4$: C, 75.41; H, 6.32. Found: C, 75.06; H, 6.34.

The di-o-trifluoromethylphenylallyl oxalate (di-o-trifluoromethylpropen-1-oxalate) was purified by three successive high vacuum molecular distillations, bp 95-11°/ 10^{-5} torr.

Anal. Calculated for $C_{22}H_{16}O_4F_6$: C, 57.66; H, 3.49. Found: C, 57.62; H, 3.68.

The di-o-ethylcinnamyl oxalate was subjected to high vacuum molecular distillation at 100°/10^{-5} torr, but it was no more than 75-85% pure by nmr spectral analysis.

Preparation of o-ethylcinnamyl formate and o-ethylphenylallyl acetate

The formate and acetate esters were prepared in the same manner as were the propargyl esters in Part I. In both cases the o-ethylphenylpropen-1-ol was used, but during the formate preparation the rearrangement to the cinnamyl isomer took place.

o-Ethylcinnamyl formate, bp 94-98°/0.5 torr.

o-Ethylphenylallyl acetate, bp 125°/12 torr. The nmr data for these esters is in Table 22.

Preparation of o-ethylcinnamyl chloride

o-Ethylcinnamyl chloride was prepared in the same manner that Gilman and Harris prepared cinnamyl chloride (80). The

product was purified by molecular distillation, bp 155-160°/12 torr. It was also isolated as a low boiling impurity from the crude oxalate, bp 20°/10^{-5} torr, nmr data in Table 22.

Separation and characterization of products

The products of the di-o-methylcinnamyl oxalate were washed from the trap with ether into a flask containing a weighed standard, either mesitylene or biphenyl. They were then analyzed for yields and collected by glpc. We used either an 8'/¼" 20% SE-30 on Chromosorb P column at temperatures between 135° and 150°, or on a 20'/¼" 20% SE-30 on Chromosorb P column at 175°. Indene was identified by glpc peak enhancement and by comparing its nmr and mass spectra with those of a commercial sample. The 4- and 7-methylindenes were collected and identified by their nmr spectra which were found to be consistent with published data (64). 1,2-Dihydronaphthalene was identified by comparison of its glpc retention time and nmr spectral data with those of a commercial sample. The nmr spectral data is recorded in Table 23.

The products from the di-o-trifluoromethylphenylallyl oxalate pyrolyses were washed from the trap with ether into a flask containing a weighed portion of mesitylene. Because of the simplicity of the nmr spectrum of the crude products, we were also able to wash the products out of the trap with a nmr solvent and analyze for product yields by adding weighed portion of methyl isobutyl ketone for an internal standard.

Both nmr spectral and glpc analyses results concurred. The glpc separation and collection was done on a 13'/¼" 20% DEGS on Chromosorb P column at ca. 145°. The products were identified by their ^{1}H and ^{19}F nmr data, Tables 21 and 23. A mass spectrum taken of a glpc collected sample of the 7-trifluoromethyl indene (70 ev) contained strong peaks at (m/e) 184, M^{+}, 151, 131, 115, 105 and 69.

The lower limit of our ability to detect indene was determined by injecting our product mixtures which had been enriched with a small amount of indene into the gas chromatograph and then attempting to collect the small peak at the retention time of indene. The collection tube was then inserted into the mass spectrometer sample holder and a spectrum taken. We found that by working with samples containing 0.5% or more indene we could get a mass spectrum identical to that of indene.

The products formed from the o-ethylcinnamyl derivatives were analyzed, separated and collected by glpc on a 20'/¼" 20% SE-30 on Chromosorb P column at ca. 165°. Yields were determined relative to an internal standard, mesitylene. The glpc retention times and nmr spectra of indene and naphthalene were identical to those of commercial samples. The other products were collected and identified by their nmr spectra, Table 23.

Commercial materials

Common reagents and solvents were purchased from Baker Chemical Co. The other chemicals used and their sources are listed in Table 19.

Table 19. Commercially available chemicals used in Part III

Compound	Source
o-Bromotoluene	Aldrich
o-Trifluoromethylbromobenzene	Aldrich
o-Ethylbromobenzene	Aldrich
Acrolien	Aldrich
Oxalyl chloride	Aldrich
1,2-Dihydronaphthalene	Aldrich
Indene	Columbia
Mesitylene	Baker
Biphenyl	Matheson, Coleman and Bell
Methyl isobutyl ketone	Mallinckrodt

Table 20. ^1H nmr spectral data of di-o-methylcinnamyl oxalate and di-o-trifluoromethylphenylallyl oxalate ($CDCl_3$)

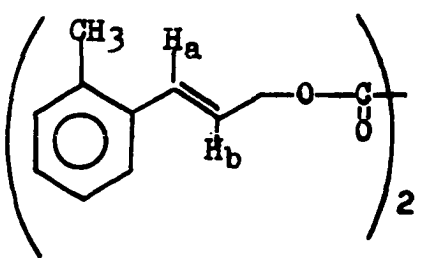
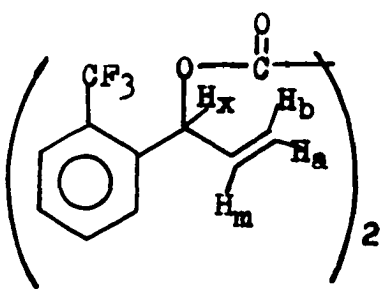
Oxalate	Resonance	Chemical Shift, δ	Pattern, Hz
	CH_3	2.31	s
	CH_2	4.91	d(J=6)
	H_b	6.18	d of t (J=6) (J=16)
	H_a	6.98	d(J=16)
	Ph	7.1-7.5	m
	H_a and H_b	5.15-5.50	m
	H_m	6.07	m
	H_x	6.84	d(J=6)
	Ph	7.25-7.85	m

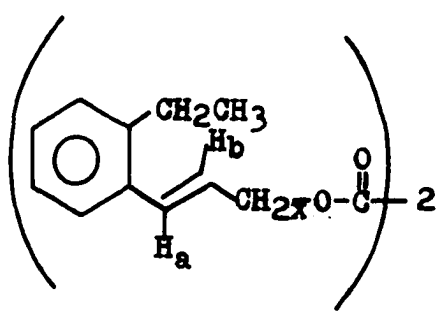
Table 21. ^{19}F nmr spectral data of the fluorinated compounds[a]

Compound	CF_3 shift	Pattern, Hz (width at ½ height)
7-Trifluoromethylindene	62.9	t(J=1.4) (3.5)
4-Trifluoromethylindene	61.1	m (2.8)
di-o-Trifluoromethyl-phenylallyl oxalate	59.5	s (6)
Trifluoromethylbenzene	63.4-63.7	s[b]

[a]The solvent was $CDCl_3$ and chemical shifts are reported in ppm relative to CCl_3F standard.

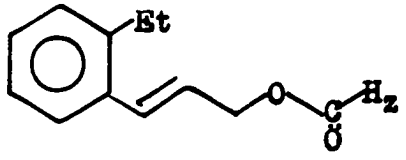
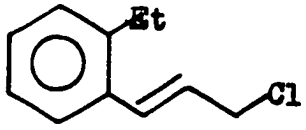
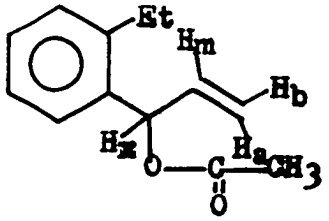
[b]Spectrum reported in (81). This data was used to determine whether our chemical shift data was reasonable.

Table 22. ^1H nmr spectral data of the o-ethylcinnamyl and o-ethylphenylallyl compounds (CCl_4)

Compound	Resonance	Chemical Shift, δ	Pattern, Hz
	H_x	4.90	d(J=7)
	H_b	6.11	d of t (J=16) (J=7)
	H_a	ca.6.9	d[a]
	CH_2	2.62	q(J=8)
	CH_3	1.08	t(J=8)

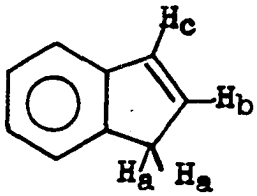
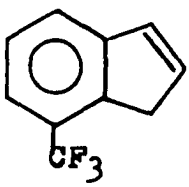
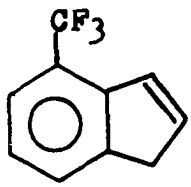
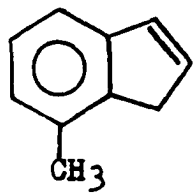
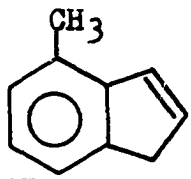
[a]Part of the pattern is obscured by the phenyl resonances.

Table 22. (Continued)

Compound	Resonance	Chemical Shift, δ	Pattern, Hz
	H_x	4.57	d of d (J=7) (J=1)
	H_b	5.90	d of t (J=7) (J=16)
	H_a	ca.6.9	d[a]
	H_z	7.81	s
	CH_2	2.47	q(J=8)
	CH_3	0.98	t(J=8)
	H_x	4.11	d(J=7)
	H_b	6.06	d of t (J=16) (J=7)
	H_a	ca.6.9	d[a]
	CH_2	2.59	q(J=8)
	CH_3	1.14	t(J=8)
	H_a	ca.5.1[b]	m[c]
	H_b	ca.5.3	m
	H_m	6.02	m
	H_x	6.55	d of t (J=5) (J=1.5)
	CH_3CO-	2.03	s
	CH_2	2.75	q(J=7)
	CH_3	1.20	t(J=7)

[b] $CDCl_3$ solvent.
[c] Pattern characteristic of terminal olefins.

Table 23. ^{1}H nmr spectral data of the products formed via pyrolyses of ortho substituted cinnamyl and phenyl allyl derivatives

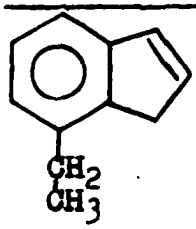
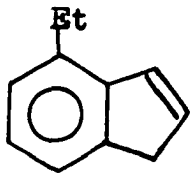
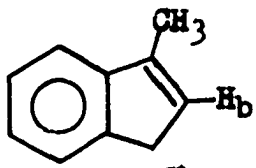
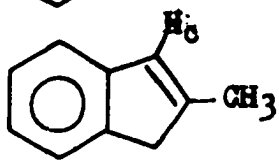
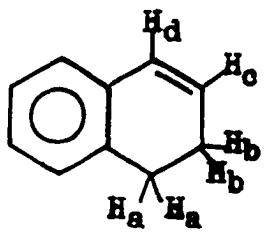
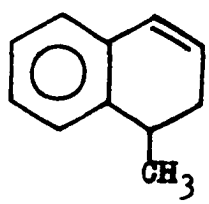
Compound	Resonance	Chemical Shift, δ	Pattern, Hz
	H_a	3.34	t(J=1.9)[a]
	H_b	6.50	d of t (J=5.2) (J=1.9)
	H_c	6.82	d of t (J=5.2)
	H_a	3.54	sextet (J=1.7)
	H_b	6.60	d of t (J=5.5) (J=1.7)
	H_c	6.86	d of t (J=5.5) (J=1.7)
	H_a	3.41	t(J=1.9)[a]
	H_b	6.70	d of t (J=5.2) (J=1.9)
	H_c	ca.7.18	m
	H_a[c] H_b[c]	3.22	t(J=2)[a,b]
	CH_3	2.35 or 2.45	s
	H_a[c] H_b[c]	3.43	t(J=2)[a,b,c]
	CH_3	2.35 or 2.45	s

[a] $J_{ab}=J_{ac}$.

[b] Consistent with published data, see (64).

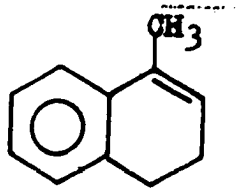
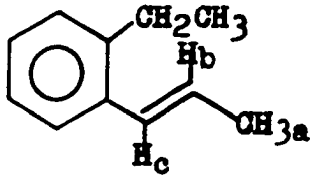
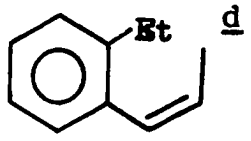
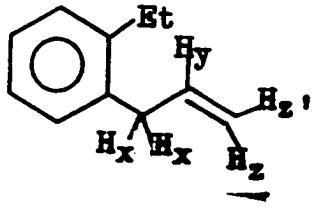
[c] Both isomers were collected together and the overlapping downfield portion of the spectrum made assignments impossible.

Table 23. (Continued)

Compound		Resonance	Chemical Shift, δ	Pattern, Hz
	d	H_a	3.35	m
		H_b	6.60	m
		H_c	ca.7.0	m
		CH_2	2.75	m
		CH_3	1.25	t(J=7)
				
	d	H_a	3.22	m
		H_b	6.15	m
		H_c	6.44	m
		CH_3	2.17	4 lines (J=2)
		H_a	2.75	t(J=7)
		H_b	2.1-2.5	m
		H_c	6.05	d of t (J=9) (J=3)
		H_d	6.45	d of t (J=9) (J=2)
		H_a	2.95	q(J=7)
		H_b	2.3	m
		H_c	5.92	d of t (J=9.5) (J=4.0)

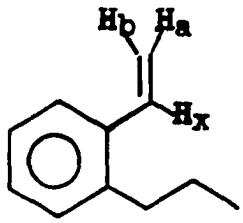
[d]Both isomers were collected together and there is some overlap of patterns.

Table 23. (Continued)

Compound	Resonance	Chemical Shift, δ	Pattern, Hz
	H_d	6.45	d of t (J=9.5) (J=1.5)
	CH_3	1.24	d(J=7)
	H_a	2.73	t(J=9)
	H_b	2.25	m
	H_c	5.80	m
	CH_3	2.05	broad s
	H_a	1.85	d(J=6)[e]
	H_b	5.7-6.4	m
	H_c	6.7	d(J=16)[e]
	CH_2	2.67	q(J=7)
	CH_3	1.17	t(J=7)
	H_a	1.69	d of d (J=7) (J=1)
	$H_b + H_c$	6.4-6.7	m
	CH_2	2.6	q(J=7)
	CH_3	1.16	t(J=7)
	H_x	3.38	d(J=6)[e]
	H_y	5.6-6.1	m
	H_z	5.15	s[e]
	H_{z1}	4.85	m

[e]Broad line(s) indicate long range coupling.

Table 23. (Continued)

Compound	Resonance	Chemical Shift, δ	Pattern, Hz
 [f]	CH_3	0.95	t(J=7)
	CH_2	1.1-1.8	m
	$H_a + H_b$	5.15-5.80	m
	H_x [g]		

[f] Collected with 2- and 3-methylindenes.

[g] Most of the pattern is obscured by the phenyl region.

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