1969

Part I. Gas phase pyrolysis of organic oxalates, Part II. Reactions of chromium(II) with organic oxalates

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69-15,637

ONG, Ching Ching (Chua), 1941-
PART I. GAS PHASE PYROLYSIS OF ORGANIC OXALATES. PART II. REACTIONS OF CHROMIUM (II) WITH ORGANIC OXALATES.

Iowa State University, Ph.D., 1969
Chemistry, organic

University Microfilms, Inc., Ann Arbor, Michigan

PART I. GAS PHASE PYROLYSIS OF ORGANIC OXALATES

PART II. REACTIONS OF CHROMIUM(II) WITH ORGANIC OXALATES

by

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

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

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Iowa State University
Ames, Iowa

1969

TABLE OF CONTENTS

PART I. GAS PHASE PYROLYSIS OF ORGANIC OXALATES

INTRODUCTION

Most organic molecules fragment when heated to a certain temperature. Because of this, pyrolysis has been widely utilized and extensively studied. Pyrolysis is industrially important, since it is extensively used in the petrochemical industry. Similarly in organic laboratories, pyrolysis is considered as one of the elegant processes for the synthetic preparation of certain organic compounds; for example, olefins from pyrolytic elimination of esters (1) and ketones from pyrolytic cleavage of acetoacetate (2) or catalytic pyrolysis of carboxylic acids or esters (3). Recent investigations have also found that certain types of organic compounds could be obtained conveniently in high yields by pyrolysis; for example, symmetrical hydrocarbons from sulfones (4), half esters from diesters (5), nitriles from cyanoacetals (6) and esters from malonic esters (7).

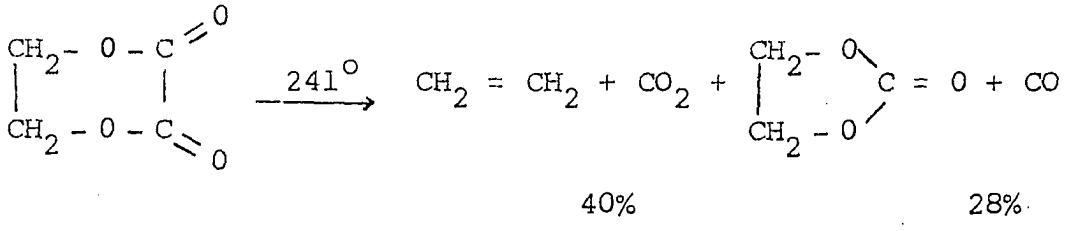
Pyrolysis of esters was first investigated in 1854 (1). Since then the pyrolysis of monocarboxylic esters, xanthates, amine oxides and halides have been extensively studied. The mechanistic aspects of ester pyrolysis and factors affecting the olefin isomer ratio have been thoroughly explored. It is well established that β-<u>cis</u> elimination occurred during the pyrolysis of monocarboxylic esters leading to olefin and

the corresponding carboxylic acid via a cyclic concerted mechanism.

Studies of the pyrolysis of a variety of oxalates have been reported. However, little attention has been devoted to the exploration of the synthetic utility or mechanistic aspects of the pyrolysis of organic oxalates.

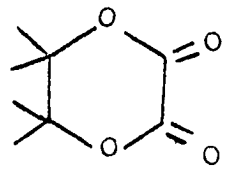
Malaguti and Cahours (8, 9) pioneered the pyrolysis of organic oxalates about 1850. They found that pyrolysis of dipentachloroethyl oxalate or di-trichloromethyl oxalate at 250-400° gave carbon monoxide, phosgene and other products. It was also reported that diethyl oxalate decomposed at 250° in a sealed tube to give carbon dioxide, carbon monoxide and olefins (10, 11). Abbott has found that monobornyl oxalate decomposed into bornyl formate and carbon dioxide upon distillation in vacuum (12). Similarly it was noted that oxalic acid when esterified with excess ethylene glycol and heated at 100° gave formate ester (13).

During the study of the pyrolysis of a series of cyclic oxalates, Tilichev has found that pyrolysis of ethylene oxalate gave ethylene and other products (14, 15). Trimethylene oxalates gave carbon monoxide, carbon dioxide and



propanal upon pyrolysis (16, 17). On the other hand, pyrolysis of 2,2-dimethyl-trimethylene oxalate gave the corresponding carbonate only (18).

Glycerol oxalate decomposed at 220-225° to give allyl alcohol and other minor products (19). A general method for the conversion of 1,2-glycols and epoxides to olefins was recently reported (20). The reaction consists of pyrolyzing the glycol in the presence of equimolar amounts of oxalic acid at 200-240°. It was suggested that not the cyclic intermediate I but instead the concerted decomposition of III or II was involved.



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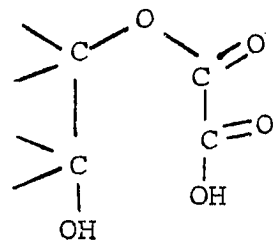

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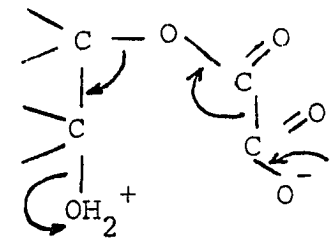


III

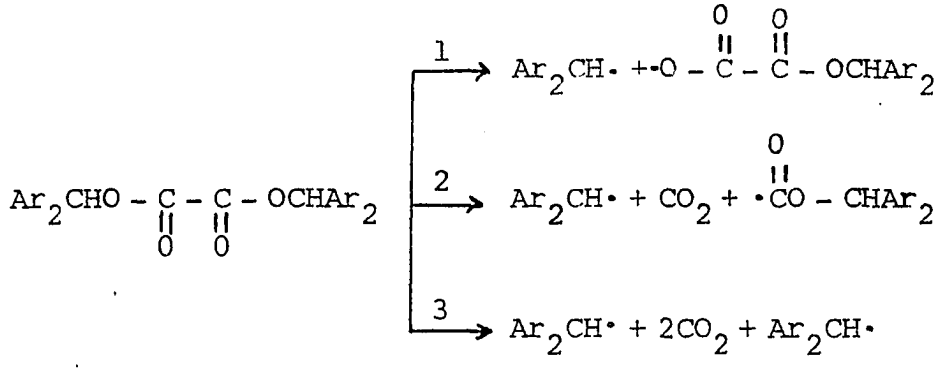
Recently, the cyclic oxalate of 2-methylene-1,3-propanediol was pyrolyzed at 450° and ca. 5% of 1,4-dimethyl-enecyclohexane was obtained (21). Trimethylene methane was postulated as the active intermediate generated.

It was found (22) that pyrolytic elimination of the cyclic oxalates of cis and trans-cyclohexane-1,2-diol gave

cyclohexene. An ion pair mechanism was postulated for the elimination reactions of these cyclic esters.

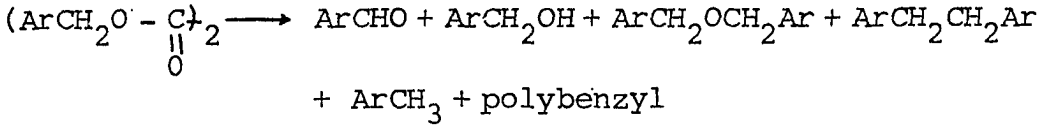
Karabatsos et al. undertook the first mechanistic studies of the thermal decomposition of dialkyl oxalates in the liquid phase (23, 24). Oxalates of tertiary alcohols decomposed readily at 140-160° to give olefins, whereas oxalates of primary and secondary alcohols resisted decomposition up to 325°. Since the composition of the olefins was more like that obtained from acid catalyzed or dimethyl sulfoxide dehydration of alcohols rather than the isomer distribution obtained from ester and xanthate pyrolyses, an ion pair mechanism was proposed.

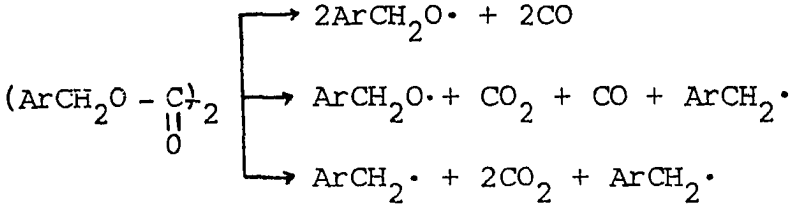
Recently, Trahanovsky, Lawson and Zabel (25, 26) and Warkentin's group (27) have independently investigated the mechanistic and kinetic aspects of thermal decomposition of dibenzhydryl oxalate. Tetraphenylethane and benzhydryl diphenylacetate were obtained when dibenzhydryl oxalate was pyrolyzed neat or in phenyl ether solution. An experiment involving deuterium labeling has indicated that the pyrolysis involves the benzhydryl free radicals as intermediates. Three possible mechanisms involving homolytic cleavage of dibenzhydryl oxalate leading to benzhydryl radical can be written. Experimental evidence has strongly suggested path 2 as the sole pathway to account for the products formed. The slow step of the thermolysis involves



concerted homolytic two-bond cleavage to form one molecule of carbon dioxide, a diarylmethyl radical and benzhydroxycarbonyl radical.

Montaudo and Purrello (28, 29) have reported that thermal decomposition of dibenzyl oxalate at 280° in a sealed tube gave benzyl alcohol, benzaldehyde, benzyl ether, toluene, bibenzyl and polybenzyl. The composition of the products varied according to the conditions used. It was suggested that the products were formed through a radical mechanism. The products could be readily accounted for from benzyloxy or benzyl radicals as follows.





$$2ArCH_2O\cdot \longrightarrow ArCHO + ArCH_2OH$$

$$2ArCH_2\cdot \longrightarrow ArCH_2CH_2Ar$$

$$ArCH_2\cdot + ArCH_2O\cdot \longrightarrow ArCH_3 + ArCH = O$$

$$ArCH_2O\cdot + ArCH_2\cdot \longrightarrow ArCH_2OCH_2Ar$$

The mass spectra of dibenzyl oxalates has recently been reported also (30).

Consideration of the thermal decomposition of organic oxalates that contain no β hydrogens raises several questions. How does the structure of the organic moiety affect the mode of decomposition? Does cage recombination occur? What are the products formed? As a continuation of the study of pyrolysis of organic oxalate containing no β hydrogens, the pyrolysis of dibenzyl oxalate was explored more carefully. Pyrolysis of dibenzyl oxalate was investigated under different conditions in this laboratory (31). Pyrolysis of dibenzyl oxalate in benzene solution over a hot column with nitrogen as a carrier gas, pyrolysis of neat dibenzyl oxalate in a flask under a nitrogen atmosphere (the product composition is shown in Table 1) (31) and pyrolysis in phenyl ether solution in a sealed tube at 300° gave non-reproducible yields of the products as previously reported. In an attempt to control the experimental conditions more exactly and to

Table 1. Pyrolysis of dibenzyl oxalate[a]

Temperature	$ArCH_2OH$	$ArCH=O$	$ArCH_2CH_2Ar$	$ArCH_2OCH_2Ar$	$ArCH_3$
350°	1.0	0.85	0.10	0.1	0.18
525°	1.0	0.97	0.25	0.1	0.18

[a]Oxalate-benzene solution over a hot column.

get more reproducible yields of the products, pyrolysis of dibenzyl oxalates was undertaken in vacuum at 660°. A series of ring substituted dibenzyl oxalates were also pyrolyzed.

Stable radicals such as benzyl, allyl and α-alkylbenzyl radicals were then generated by pyrolysis of appropriate oxalates in the gas phase. Several aspects of free radical chemistry, stereospecificity of radical coupling and intromolecular radical cyclization were also investigated.

RESULTS AND DISCUSSION

The oxalic esters used in this study are prepared in fairly high yield from oxalic acid or oxalyl chloride and the corresponding alcohol. The infrared spectra of the oxalates possess a distinctive doublet in the carbonyl region, 1790-1760 and 1755-1740 cm^{-1} in chloroform. Physical properties and methods of preparation of these oxalates are listed in Tables 16, 17, 18 and 19.

Pyrolysis of Ring Substituted Dibenzyl Oxalates

The ring substituted dibenzyl oxalates were readily decomposed under vacuum at 650-660^{o} in good yields (40-75%) to the corresponding bibenzyls (Table 2). Nmr analysis of the pyrolysates showed that at least 90% of the product was bibenzyl, small amounts (<5%) of the recovered oxalate, the corresponding benzyl alcohol, benzaldehyde, toluene and benzyl ether. No effort was made to determine the yields of these by-products. In large scale runs, oxalates were usually pyrolyzed in gram quantities during a 1-2 hour period. The pure bibenzyl was obtained by chromatography of the crude pyrolysate on a silica gel colmun followed by recrystallization of the bibenzyl. In small scale runs, yields of bibenzyls were determined by nmr or glpc analysis using an internal standard. The identity of the bibenzyls were confirmed by their melting points or nmr spectra also (four

Table 2. Gas phase pyrolysis of dibenzyl oxalates ($RCH_2OCOCOOCH_2R$) to bibenzyls (RCH_2CH_2R)[a]

R	Yields of bibenzyls, %[b]	Mp of bibenzyls, °C	Literature mp, °C
C_6H_5	59,61	51-52	51.5-52.5[c]
p-ClC_6H_4	69,66	100-101	100[d]
o-ClC_6H_4	69,73,76[e]	59-61	62[d]
m-ClC_6H_4	62,58,66[e]	48-50	52[d]
p-BrC_6H_4	40[e],44[e]	112-114	114[d]
p-FC_6H_4	72,72[e]	87-89	90[f]
p-$CH_3C_6H_4$	47,51,57[e]	78-80	79-81[g]
p-NCC_6H_4	44[h],43[h]	196-198	198[i]
α-Naphthyl	46[e],52[e]	159-161	162[j]
m-$O_2NC_6H_4$	-[k]	-	-
p-$CH_3OC_6H_4$	-[l]	-	-

[a]The head temperature was 110-145°; the pressure of the system was 0.07-0.1 mm.

[b]Isolated yields of recrystallized bibenzyls unless otherwise noted.

[c]Source: (32).

[d]Source: (33).

[e]Yield obtained by addition of a standard (dimethyl oxalate) and nmr analysis.

[f]Source: (34).

[g]Source: (35).

[h]Yield obtained by addition of a standard (bibenzyl) and glpc analysis.

[i]Source: (36).

[j]Source: (37).

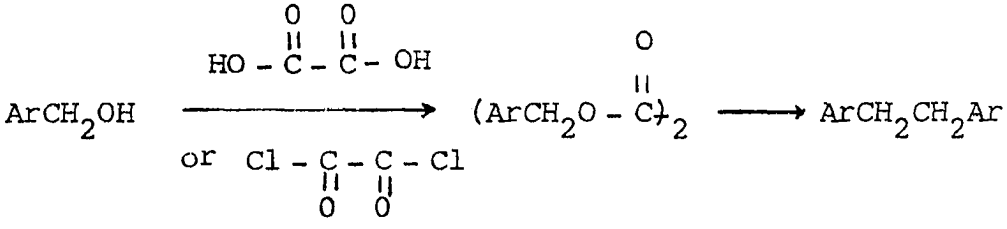
[k]From nmr analysis, at least two different bibenzyls were in poor yield.

[l]NMR analysis of product mixture showed no bibenzyl present.

proton singlet at δ2.6-3.0, except for the case of p,p'-dicyanobibenzyl which was too insoluble to obtain an nmr spectrum).

The striking difference in results obtained from oxalate pyrolysis under vacuum compared to those of conventional flow system reflects the uniqueness of vacuum pyrolysis. When slightly volatile compounds are pyrolyzed under vacuum, the reaction can be made to take place in the vapor phase more readily and thus the reaction conditions can be controlled more exactly to give reproducible yield of products.

Bibenzyls are usually prepared by the Wurtz reaction or by reduction of Grignard reagents. p,p'-Dicyanobibenzyl could not be prepared from a Grignard reagent (36) and was obtained in poor yields by other reactions (38), but was formed from oxalate pyrolysis in good yield. Generally speaking, pyrolysis of dibenzyl oxalates under vacuum is a good way for converting benzyl alcohols to bibenzyls through oxalates, (except m,m'-dinitrobibenzyl and p,p'-dimethoxylbibenzyl) since



anhydrous conditions are not required and the reagents used are neither expensive nor explosive.

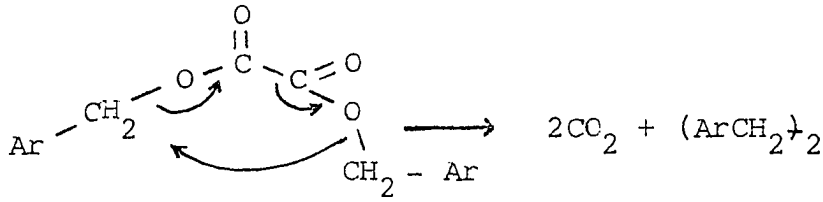
Oxalates containing polar functional groups like the electron donating p-methoxyl are quite labile and tend to decompose before vaporizing. Recently, Fields and Meyerson (39, 40) have observed that nitro-arene bond cleavage occurred above 400°. It is also well established that nitroaromatics are quite explosive at high temperatures (41). The nmr spectrum of the pyrolysate of di-m-nitrobenzyl oxalate showed two peaks centered at 3.0δ, corresponding to the chemical shift for the methylene protons of bibenzyls. A mixture of bibenzyls was probably formed which was due to the fragmentation of the nitro-arene bond either prior to oxalate decomposition or after bibenzyl formation.

Among the halogen substituted dibenzyl oxalates, the yield of p,p'-dibromobibenzyl was quite low. Since the carbon-bromine bond is weaker than carbon-chlorine or carbon-fluorine bonds, it is quite likely that bond cleavage occurred during pyrolysis leading to decomposition products. Indeed the pyrolysate of di-p-bromobenzyl oxalate was quite dark.

In the case of di-p-methylbenzyl oxalate, the p-methylbenzyl radical underwent disproportionation as well as coupling. Aside from bibenzyl, a substantial amount of p-xylene and some polymeric white material were also obtained. The polymeric substance was insoluble in common organic solvents, and was probably the poly-p-xylylene, since its

solubility properties agreed with those reported (42). E. Leonard has also obtained poly-p-xylylene upon pyrolysis of di-p-methylbenzyl sulfone through p-xylylene diradicals formed from disproportionation of the p-methylbenzyl radicals generated during the course of pyrolysis. It is likely that the poly-p-xylylene obtained during the pyrolysis was not the product formed directly from the oxalate but from the further carbon-carbon bond cleavage of p,p'-dimethylbibenzyl. However it has been shown (42) that under our experimental conditions, carbon-carbon bond in p,p'-dimethylbibenzyl did not rupture and that no poly-p-xylylene was obtained at 600-700^{o} by pyrolysis of this bibenzyl.

The formation of bibenzyls from the pyrolysis of dibenzyl oxalates is most reasonably accounted for by the coupling of benzyl radicals. However the alternative formation of the bibenzyl intramolecularly through a cyclic mechanism cannot be ignored.



In order to ascertain whether the formation of bibenzyls is intermolecular or intramolecular, benzyl benzyl-α,α-d_2 oxalate and benzyl p-chlorobenzyl oxalate were respectively

pyrolyzed under the same conditions as other oxalates. The stability of the bibenzyl under the reaction conditions was also established by passing p-chlorobibenzyl over the hot tube since only 12% of each symmetrical bibenzyl were obtained. Since the residence time of the p-chlorobibenzyl is longer than that of p-chlorobibenzyl formed from the oxalate, decomposition of the benzyl p-chlorobenzyl oxalate *via* an intramolecular pathway should give mainly p-chlorobibenzyl, but an intermolecular pathway should give bibenzyl, p-chlorobibenzyl and p,p'-dichlorobibenzyl in the ratio 1: 2: 1. The product distributions of oxalate pyrolysis were determined by glpc analysis. The p,p'-dichlorobibenzyl, p-chlorobibenzyl and bibenzyl were formed in the ratio 1: 2.04 : 1. The intermolecular nature of bibenzyl formation was further supported by the deuterated dibenzyl oxalate. The isotope distributions of the bibenzyls were determined by mass spectral analysis (Table 3). The experimental results are in good agreement with that calculated for an intermolecular process.

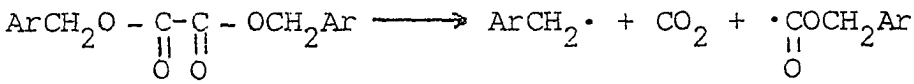
Similar to the thermal decomposition of dibenzhydryl oxalates (26), dibenzyl oxalates probably undergo two bond cleavage to form benzyl radicals, carbon dioxide and benzyloxycarbonyl radical, which rapidly decarboxylated at high temperature to give benzyl radical and carbon dioxide.

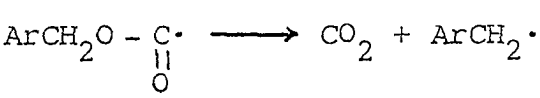
Table 3. Isotopic distributions in bibenzyl obtained from the pyrolysis of benzyl benzyl-α,α-$\underline{d}_2$ oxalate[a]

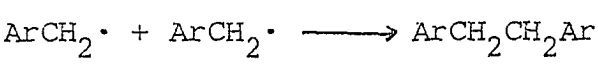
	$\underline{d}_0$	$\underline{d}_1$	$\underline{d}_2$	$\underline{d}_3$	$\underline{d}_4$
Experimental	26.4	14.2	37.3	10.3	11.8
Calculated Intermolecular	29.3	11.7	39.1	7.6	12.3
Intramolecular[b]	8.3-18.9	16.7-21.6	54.7-70.1	0-3.8	0-6.2

[a]The oxalate was 8.3% $\underline{d}_0$, 21.6% $\underline{d}_1$, and 70.1% $\underline{d}_2$.

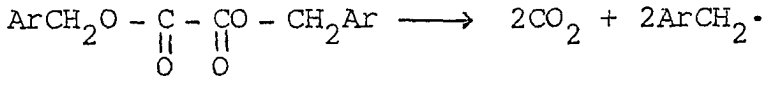
[b]With no more than 50% decomposition of the bibenzyl to benzyl radicals which would combine statistically.







An alternative mechanism is three bond cleavage to give two moles of carbon dioxide and two benzyl radicals.



These two mechanisms are consistent with the intermolecular nature of the pyrolysis.

No phenylacetate was obtained in the case of dibenzyl oxalate pyrolysis which is in contrast to the benzylhydryl

diphenylacetate obtained at low temperature from dibenzylhydryl oxalate. The benzyloxycarbonyl radical must readily decarboxylate at high temperatures. Pyrolysis of benzyl benzhydryl oxalate in phenyl ether at 245° also gave considerable amount of benzyl diphenylacetate (26). Recently alkoxycarbonyl radicals were also generated from the thermal decomposition of tritylazocarboxylates by Trahanovsky and Zabel (25). Several products (25) derived from the alkoxycarbonyl radicals were also isolated. These suggested that alkoxycarbonyl radical possesses sufficient stability to be trapped. It has been found that the alkoxycarbonyl radicals generated from decomposition of benzyl or ethyl t-butylperoxy oxalates and di-t-butyl monoperoxy oxalate (43, 44) were stable enough to escape from the solvent cage. Zabel (25) has also mentioned that there is an obvious discrepancy between Bartlett's work and their results concerning attack of alkoxycarbonyl radicals on aromatic solvent.

Traces of methyl acetate was found by Kebarle and Lossing (45) in a mass spectrometric study of the mercury-photosensitized decomposition of methyl formate presumably produced by the coupling of methyl radicals with methoxycarbonyl radicals. Ethoxycarbonyl radicals were also

$$CH_3\cdot + CH_3O-\overset{\overset{O}{\|}}{C}\cdot \longrightarrow CH_3O-\overset{\overset{O}{\|}}{C}-CH_3$$

trapped from photolysis of ethylcyano formate (46). It was also proposed that benzyl formate (61%) and toluene (39%) were obtained by organotin hydride reduction of benzyl chloroformate via an intermediate benzyloxycarbonyl radical (42). On the other hand, tri-n-butyl tin hydride reduction

$$ArCH_2O-\underset{\underset{O}{\|}}{C}-Cl + (Ar)_3Sn\cdot \longrightarrow ArCH_2O-\underset{\underset{O}{\|}}{C}\cdot + Ar_3SnCl$$

$$ArCH_2O-\underset{\underset{O}{\|}}{C}\cdot \longrightarrow ArCH_2\cdot + CO_2$$

$$ArCH_2O-\underset{\underset{O}{\|}}{C}\cdot + Ar_3SnH \longrightarrow ArCH_2O-\underset{\underset{O}{\|}}{C}-H + Ar_3Sn\cdot$$

$$ArCH_2\cdot + Ar_3SnH \longrightarrow ArCH_3 + Ar_3Sn\cdot$$

of ethyl chloroformate gave only ethyl formate (47). Presumably the greater the stability of the alkyl radical (R·) formed, the greater will be the rate of decarboxylation of the alkoxycarbonyl radical. Thynne and Gray (48, 49) have demonstrated that at 120-185°, methoxycarbonyl radical ($CH_3O-\overset{\overset{O}{\|}}{C}\cdot$) broke down to a methyl radical and carbon dixoide quantitatively. Similarly, about 87-98% of the t-butoxycarbonyl radicals escaped from solvent cage decarboxylated, while less than 20% of the ethoxycarbonyl radicals escaping from the solvent cage decarboxylated (43, 44).

Less is known about the nature of alkoxycarbonyl radical, although the stability and reactivity of its close

related isomeric radical, acyloxy radical ($R-\overset{O}{\overset{\|}{C}}-O\cdot$) has been extensively studied. Gray and Thynne (50) have considered the thermochemistry and reactivity of alkoxycarbonyl radicals recently. They pointed out that the activation energy for decomposition of the methoxycarbonyl radical is perhaps somewhat greater than the value of 1-2 kcal suggested for the decarboxylation of acetyloxy radical. This is in accord with the relative bond strengths calculated for methoxycarbonyl radical (alkyl-oxygen bond, 10.9 kcal) and acetoxy radical (alkyl-carbonyl carbon bond, 17.5 kcal) respectively (50).

Pyrolysis of Di-α-alkylbenzyl Oxalates

Karabatsos and co-workers (23) have studied the thermal decomposition of a series of dialkyl oxalates that possesses β hydrogens in liquid phase. These oxalates underwent elimination to give the isomeric olefins. Pyrolysis of ring substituted dibenzyl oxalates under vacuum gave exclusively bibenzyls resulting from coupling of benzyl radicals. These oxalates pyrolyzed were systems containing no β hydrogens. It seemed worthwhile to explore the pyrolysis of dibenzyl oxalates possessing β hydrogens, i.e. di-α-alkylbenzyl oxalates. Consideration of the mechanistic aspects of the pyrolysis of dibenzyl oxalates with β hydrogens raises several questions. What

is the mode of decomposition of this type of oxalate? Will elimination occur during pyrolysis? Could the stable benzyl radical be generated? What is the fate of this benzyl radical? Can this benzyl radical couple, disproportionate or undergo β scission if there is a β-alkyl group present?

During the last decade research of radical chemistry has been quite extensive. However, most workers have ignored problems of stereochemistry or have not employed systems where stereochemical problems arise. In view of the essence of stereochemistry in radical reactions (51-54) the stereospecificity of radical coupling was also studied.

Pyrolysis of di-α-methylbenzyl oxalate

Glpc and nmr analyses of the pyrolysate of di-α-methylbenzyl oxalate at 570° showed that styrene, benzaldehyde, dl and meso-2,3-diphenylbutanes were the major products. A few unknowns and possibly the formate of α-methylbenzyl alcohol were also formed. Considerable amounts of styrene were obtained in different runs. The styrene may come possibly from a concerted cyclic elimination pathway or by disproportionation of the α-methylbenzyl radical generated. If styrene was formed through disproportionation then ethylbenzene should be formed also. From the nmr spectrum of the pyrolysate, there was only a negligible amount of ethylbenzene compared to styrene. The styrene probably came

from a cyclic elimination pathway. A series of pyrolyses was undertaken at different temperatures to ascertain if there is any dependency of product distribution with pyrolysis temperature (Table 4). Benzaldehyde must be formed from β scission of α-methylbenzyloxy radical which occurred from oxygen-carbonyl carbon bond cleavage of the oxalate or benzyloxycarbonyl radical.

Since the desired 2,3-diphenylbutanes were obtained, the stereospecificity of the radical coupling reaction was determined. The stability of 2,3-diphenylbutanes at different temperatures was also established (Table 5). At 480°, the meso-2,3-diphenylbutanes did not isomerize. A relative ratio of meso to dl-2,3-diphenylbutanes equal to 52/48 was obtained from coupling of α-methylbenzyl radicals at 480° (Table 6).

α-Methylbenzyl radicals have been generated from several sources and under a variety of conditions. In each case, the radicals coupled to give the diastereomeric 2,3-diphenylbutanes (Table 7). Some of the earlier data are not in good agreement with the latest ones which was probably due to the inaccurate methods of analysis used. In our hands, when 2,3-diphenylbutanes obtained from the reaction of α-methylbenzyl chloride and its Grignard reagent (55) were analyzed by glpc, a meso-dl ratio of 51/49 was obtained. This coincides quite well with most data reported

Table 4. Ratios of styrene and 2,3-diphenylbutanes from pyrolysis of di-α-methylbenzyl oxalate at different temperatures

Temperature	Mole ratio of styrene to 2,3-diphenylbutanes	Remark
400°	8.72	incomplete decomposition
450°	4.85	incomplete decomposition
500°	4.87	incomplete decomposition
570°	5.43	
650°	9.0	

Table 5. Pyrolysis of meso-2,3-diphenylbutane

Temperature	% of dl isomer present in the pyrolsate
450°	none
480°	none
500°	less than 5%
540°	15%

Table 6. Relative ratios of meso and dl-2,3,diphenylbutanes obtained from pyrolysis of di-α-methylbenzyl oxalate at 480°

Run	meso/dl
I	52.1/47.9
II	51.9/48.1
Average	52/48

Table 7. Literature data of the stereoisomer ratio of 2,3-diphenylbutanes formed from coupling of α-methylbenzyl radical

Reaction	meso/dl	Reference
PhEt + Ac_2O_2	50/50	(56)
PhEt + $(t\text{-BuO}\cdot)_2$	60.5/39.5	(57)
PhEt + Bz_2O_2	50/50	(58)
PhEt + Bz_2O_2	51.2/48.8	(59)
PhEt + $(t\text{-Bu-OO-}\overset{\overset{O}{\|}}{C}\cdot)_2$	50/50	(60)
PhEt + $(t\text{-BuO}\cdot)_2$	50/50	(60)
PhEt + $(t\text{-Bu-O}\cdot)_2$	51.3/48.7	(61)
PhEt + Ac_2O_2	60.1/39.9	(61)
$PhCH_2MgCl$ + $PhCH_2Cl$	68/32	(61)
PhEt + $(t\text{-BuO}\cdot)_2$	50.4/49.6	(62)
$PhCH_2MgCl$ + $PhCH_2Cl$	50/50	(62)
Decomposition of $(PhCH(CH_3)N{=}N\cdot)_2$ (DMF as solvent)	50/50	(63)
Decomposition of $(PhCH(CH_3)N{=}N\cdot)_2$ (no solvent)	41.5/58.5	(63)
Electrolysis of $Ph\text{-}CH(CH_3)\overset{+}{N}(CH_3)_3\overset{-}{NO_3}$	46/54	(63)
Decomposition of $(PhCH(CH_3)CO_2\cdot)_2$	51.4/48.6	(64)

including that of oxalate pyrolysis obtained from this study.

The fact that approximately equal amounts of meso and dl diastereomers were obtained from the coupling of α-

methylbenzyl radicals under a variety of conditions, indicates that no stereochemical preference was observed during coupling reaction. This reflects also that there is a negligible difference in the activation energy for the formation of the two isomers. Thus the coupling of the radicals formed both diastereomers with $\Delta\Delta F^*$, $\Delta\Delta H^*$ and $\Delta\Delta S^*$ equal to zero within experimental error (60).

Stereochemically, the coupling of two free radicals is usually assumed to be a completely random process, when cage recombination does not occur. If steric and polar effects do not take part then two similar radicals would dimerize to two diastereomers in equal amounts as in the case of α-methylbenzyl radical. Several cases of stereospecific coupling reactions in the literature have been reported (Table 8). These were usually attributed to steric factors.

Pyrolysis of di-α-trifluoromethylbenzyl oxalate

Polar effects could influence the stereospecificity of a radical reaction. To examine this possibility, di-α-trifluoromethylbenzyl oxalate was pyrolyzed to generate the desired α-trifluoromethylbenzyl radical.

Glpc analysis of the pyrolsate of di-α-trifluoromethylbenzyl oxalate obtained at 650° indicated the presence of at least five components and the recovered oxalate. One of

Table 8. Reported stereoisomer composition of dimers produced in various radical reactions

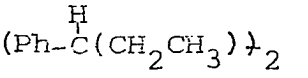
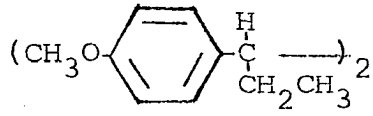
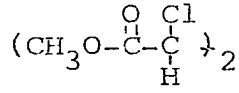
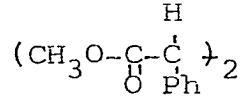
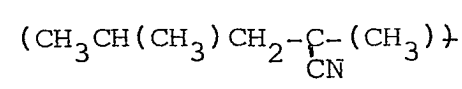
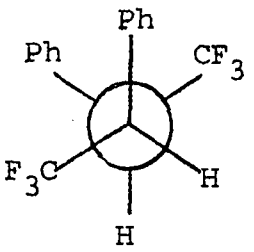
Reaction	Dimer	meso/dl	Reference
Propylbenzene + Ac_2O_2		50/50	(65)
p-Methoxy-n-propylbenzene + Ac_2O_2		50/50	(65)
Methyl chloroacetate + Ac_2O_2		50/50	(66)
Methyl phenylacetate + Ac_2O_2		50/50	(67)
$PhCH_2OR$ + (t-Bu-O)$_2$	PhCH(OR)CH(OR)Ph	50/50	(67)
Isobutylbenzene + Ac_2O_2 or (t-Bu-O)$_2$	PhCH(CH$(CH_3)_2$)CH(CH$(CH_3)_2$)Ph	55.5/44.5	(62)
Neopentylbenzene + Ac_2O_2 or (t-Bu-O)$_2$	PhCH(C$(CH_3)_3$)CH(C$(CH_3)_3$)Ph	57.4/42.6	(62)
2,2'-azo-bis-2-dimethylvaleronitrile		50/50	(68)

Table 8 (Continued)

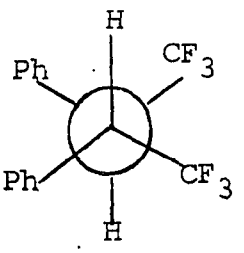
Reaction	Dimer	meso/dl	Reference
Dimethyl succinate + Ac_2O_2	$(CH_3O-\overset{O}{\overset{\|}{C}}-CH_2CH(\overset{O}{\overset{\|}{C}}OCH_3)\rightarrow_2$	98/2	(65)
Decomposition of $(Ph-\overset{CH_3}{\overset{\|}{\underset{CH-(CH_3)_2}{\underset{\|}{C}}}}-N\rightarrow_2$	$(Ph\overset{CH_3}{\overset{\|}{C}}CH-(CH_3)_2\rightarrow_2$	50/50	(69)
$Ph(CH_2)_4CH_3$ + $(\underline{t}\text{-}BuO\rightarrow_2$	$(Ph-\overset{H}{\overset{\|}{C}}\longrightarrow\rightarrow_2$ $CH_2CH_2CH_2CH_3$	50/50	(70)
4-Phenyl-2-butanone + $(\underline{t}\text{-}BuO\rightarrow_2$	$(CH_3-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{\|}{C}}\rightarrow_2$ CH_2Ph	100/0	(71)
Ethyl 3-phenylpropionate + $(\underline{t}\text{-}BuO\rightarrow_2$	$(EtO_2C-\overset{CH_2Ph}{\overset{\|}{C}}\longrightarrow\rightarrow_2$ H	100/0	(71)

these compounds is a low boiling liquid with a pungent odor. Its identity was not established but was believed to be β,β-difluorostyrene upon comparison of its nmr spectrum with the pyrolysate obtained from di-α-perfluoroethylbenzyl oxalate. Four of the other components were separated by glpc collection. Component A (mp 73-75°) and B (mp 156-158°) were assigned as the dl and meso-2,3-diphenyl-1,1,1,4,4,4-hexafluorobutane (DPHFB) respectively. The structures of these isomers were further confirmed by nmr, ir and mass spectra and elemental analysis. It is well recognized that in general (72), the more symmetrical compound has a higher melting point than the related less symmetrical compound. In our case the assigned meso-isomer also has a higher melting point than the dl-isomer.

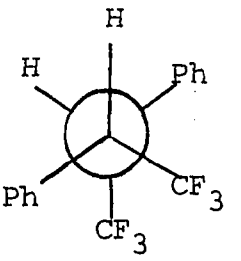
Nmr has been used to study the hindered rotation in substituted ethanes but also the conformations of the cis and trans-isomers of cyclic compounds (73). The aromatic ring protons of trans-1,2-diphenylcyclopentane appear as a singlet; while in the cis-isomer, the aromatic protons are more shielded and appear as a doublet. The meso-DPHFB also has the aromatic protons appear as a sharp singlet while that of the dl-isomer are more complex and appear at higher field, presumably due to substantial phenyl ring interactions. This indicates that the predominant conformers of the dl-isomer is either IV or V.



IV

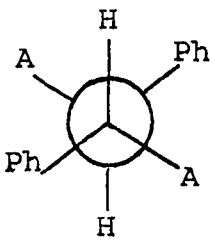


V

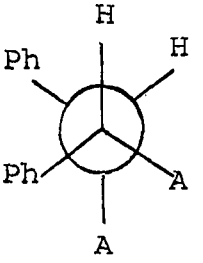


VI

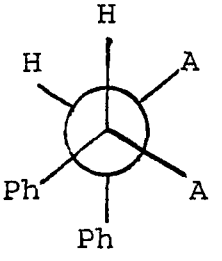
Recently, Sawatzky and coworkers (74, 75) have investigated the conformational preferences of a system pertinent to DPHFB, 2,5-dimethyl-2,5-dimethoxyl-3,4-diphenylhexane (DDDPH). They found that for the meso isomer the conformer



VII

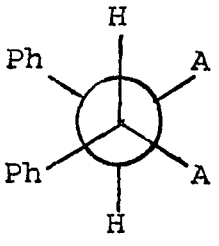


VIII

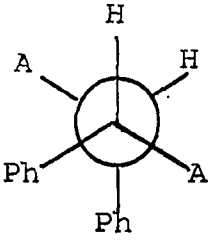


IX

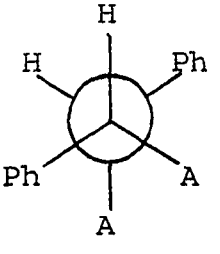
$$A = -\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-OCH_3$$



X



XI



XII

VIII is more stable than IX by 1.7 kcal/mole and for the dl-isomer, conformer X is more stable than XI or XII by 1.9 kcal/mole by nmr technique. From this previous work, one might envision that substantial conformational preference also exists in the dl-DPHFB as shown by its nmr spectrum (Figure 4).

The meso/dl ratio of the DPHFB obtained from the pyrolysis of di-α-trifluoromethylbenzyl oxalate varied with temperature; for example at 650°, meso/dl was 45/55, at 570°, meso/dl was 40/60. This is because interconversion of the meso-dl isomers occurred quite readily at high temperatures (Table 9). The stability of the DPHFB isomers was then established. At 500°, there was negligible amount of isomerization. Glpc analysis of the pyrolysate of di-α-trifluoromethylbenzyl oxalate run at 500°, indicated that the dl/meso of DPHFB formed was 71/29. This striking difference of meso-dl ratio obtained, compared to that of the equal diastereomeric forms of 2,3-diphenylbutanes from radical coupling is quite significant and requires explanation. This considerable stereoselectivity which occurred in the dimerization of α-trifluoromethylbenzyl radicals indicates that there is a substantial difference in the activation energy leading to the different diastereomers. Since the

Table 9. Pyrolysis of 2,3-diphenyl-1,1,1,4,4,4-hexafluorobutanes

Isomer	Temperature	dl/meso
meso	630°	_a
meso	570°	58/42
dl	570°	67/33
meso	500°	5/95

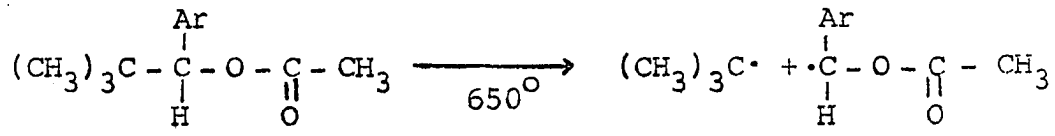
[a]Most of the hydrocarbons was destroyed.

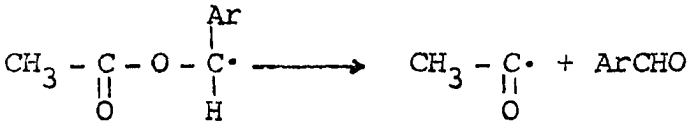
trifluoromethyl group is not much larger than the methyl group, steric factors are excluded. The conformational preference observed is likely due to the polar nature of the trifluoromethyl groups present.

From the synthetic point of view, the formation of DPHFB by the pyrolysis of di-α-trifluoromethylbenzyl oxalate is of considerable significance. A yield of 40% was obtained at 650°. Prior to our preparation, these compounds were unknown. A Grignard coupling reaction is a possible pathway to these fluorinated hydrocarbons. However the literature has shown that α-fluorinated Grignard reagents are quite unstable and difficult to work with (76).

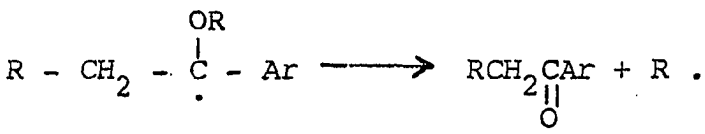
Since primarily fragmentation products of the intermediate radicals were obtained from the pyrolysis of other di-

α-alkylbenzyl oxalates, no stereochemical results on the radical coupling can be obtained. Attempts to prepare di-α-t-butylbenzyl oxalate were unsuccessful. α-t-Butylbenzyl acetate was pyrolyzed in the hope of obtaining α-t-butylbenzyl radical. However no dimerization products were obtained. Instead, pyrolysis of α-t-butylbenzyl acetate gave considerable amounts of benzaldehyde and other unidentified products. The acetate presumably undergoes a carbon-carbon bond cleavage to form a t-butyl radical and an α-substituted benzyl radical. Further β scission of the benzyl radical



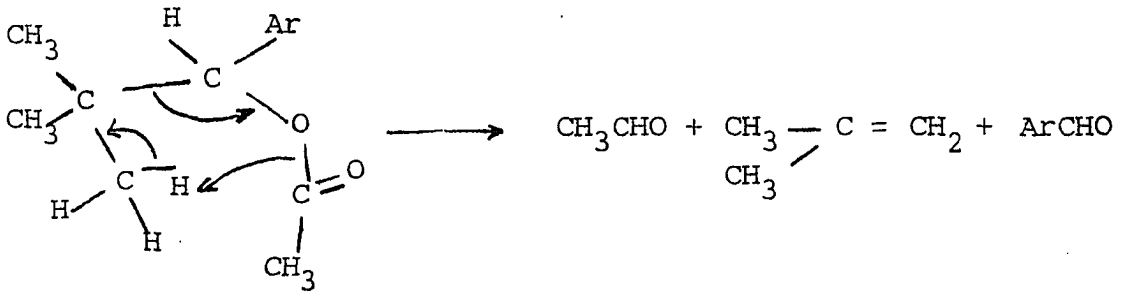


gives benzaldehyde and acetyl radical. The stability of the resulting benzyl and t-butyl radicals formed is probably the main driving force. This mode of cleavage of the α-substituted benzyl radical is analogous to that previously reported (77).



An alternative pathway for the benzaldehyde formation

is the cyclic concerted reaction.



Pyrolysis of di-α-ethylbenzyl oxalate and di-α-isopropylbenzyl oxalate

The yields and relative ratios of the products obtained respectively from the pyrolysis of di-α-ethylbenzyl oxalate and di-α-isopropylbenzyl oxalate at 570° are summarized in Tables 10 and 11 respectively. Considerable amounts of olefins which most probably came from a cyclic concerted elimination pathway of the oxalate were obtained. In each case, olefins formed from fragmentation of the intermediate α-alkylbenzyl radicals were also obtained.

Pyrolysis of di-α-perfluoroethylbenzyl oxalate

The nmr and ir spectra of the pyrolysate of di-α-perfluoroethylbenzyl oxalate obtained at 650°, were the main features of β,β-difluorostyrene (78). Nmr analysis of the pyrolysate showed that 1.36 mole of styrene was formed per mole of oxalate pyrolyzed. Glpc analysis of the pyrolysate showed the presence of at least three high boiling components in small amounts. Two of them might be the

Table 10. The approximate yields[a] and relative ratios of the products obtained from the pyrolysis of di-α-ethylbenzyl oxalate at 570°

	trans-β-methylstyrene	cis-β-methylstyrene	unknown	unknown	unknown	styrene
relative ratio	1	0.037	0.126	0.063	.03	0.43
mole / mole of oxalate	0.76	0.026	0.09	0.045	.02	0.31

[a]Based on nmr analysis, using dimethyl oxalate as the internal standard.

Table 11. Relative ratios and yields[a] of the products obtained from the pyrolysis of di-α-isopropylbenzyl oxalate at 570°

	styrene	unknown	cis-β-methylstyrene	trans-β-methylstyrene	β,β-dimethylstyrene
relative ratio	.0055	.012	.061	0.62	1
mole / mole oxalate	--		--	0.36	0.905

[a]Based on nmr analysis, using dimethyl oxalate as the internal standard.

dimerized products of the intermediate radicals. Since these two components were only present in small amounts no attempt was made to establish their identities. The β,β-difluorostyrene undoubtedly was formed from the β scission of the α-perfluoroethylbenzyl radical.

Pyrolysis of di-α,α-dimethylbenzyl oxalate

A quantitative yield of α-methylstyrene was obtained from pyrolysis of di-α,α-dimethylbenzyl oxalate. The expected tertiary radical was not generated; instead, the oxalate undergoes pyrolytic elimination leading to the olefin. This is quite similar to the results obtained by Karabatsos et al. (23) from the pyrolysis of oxalates of tertiary alkyl alcohols. The olefin presumably came from a concerted cyclic pathway while an ion pair mechanism proposed in previous work (23, 24) could also be considered.

The results obtained from the pyrolysis of di-α-alkylbenzyl oxalates are quite different from those dibenzyl oxalates having no β hydrogens. Upon pyrolysis, the di-α-alkylbenzyl oxalates undergo homolytic cleavage to give the corresponding radicals as well as olefin formation. The olefins probably came from a cyclic concerted pathway similar to acetate pyrolysis (1). An ion pair mechanism as proposed by Karabatsos et al. in their study of dialkyl oxalate pyrolyses cannot be ruled out entirely (23, 24). The intermediate

α-alkylbenzyl radicals undergo β scission exclusively to give olefins rather than coupling if the radicals have β-alkyl substituent present. The β scission of alkyl radicals is quite related to those of fragmentation of secondary or tertiary alkoxy radicals. Greene (79) and Bacha and Kochi (80) have concluded that the relative ease of ejection of alkyl radicals in the alkoxy radicals is isopropyl > ethyl > methyl. This is in the order of increasing carbonium ion or radical stability. Aside from recombination and fragmentation radicals could also undergo disproportionation. In most of the di-α-alkylbenzyl oxalates pyrolyzed no detectable amounts of disproportionation products were found. This is quite similar to the case of alkoxy radicals. It is well documented that tertiary alkoxy radicals undergo β scission more readily at higher temperature. At lower temperature, disproportionation of the alkoxy radicals is more favorable, since β scission is a more endothermic process.

Fragmentation of alkyl radicals, especially di-α-alkylbenzyl radicals have not been extensively investigated. Only a few scattered examples are cited in the literature such as fragmentation of lower alkyl radicals (81), bond scission of aryl substituted alkyl radicals during high temperature cracking of alkylbenzene (82) and reversibility of radical addition to olefins (83, 84). Recently, Bartlett and McBride (85) have generated the 1-phenyl-1-methyl-isobutyl

radical. This radical undergoes exclusively dimerization and disproportionation. The fact that we have obtained exclusively the β-scission products is undoubtedly due to the high temperature process.

It is quite significant that even the α-perfluoroethylbenzyl radical undergoes predominantly β scission similar to the hydrogen analogue. So far no study concerning the fragmentation of α-perfluoroalkylbenzyl radicals has been reported. However it is well documented that the perfluoroalkyl radicals behave somewhat similarly to the alkoxy radicals. They can undergo disproportionation as well as β scission (86, 87). Heptafluoropropyl radicals generated from the photolysis of perfluoro-di-n-propyl ketone also undergo β scission (88).

Pyrolysis of Diallyl Oxalates

Pyrolysis of diallyl oxalate

The stability of the radical generated from oxalates having no β hydrogens affects the ease of thermal decomposition as shown by dibenzhydryl and dibenzyl oxalates. Since the allyl radical has similar resonance stability as the benzyl radical (77, 89, 90, 91, 92), diallyl oxalate was pyrolyzed to generate allyl radicals.

Biallyl was obtained from pyrolysis of diallyl oxalate. In an effort to optimize the yield of biallyl, a series of

runs under different conditions was carried out (Table 12). Since the fluid dynamics of the vacuum pyrolysis flow system is quite complicated, no attempt was made to treat these results in any theoretical sense. The following facts were drawn from the results.

1. Higher pressures of the system lead to longer retention times in the hot tube; thus more destruction of organic molecules and more complete decomposition of the oxalate occurs.

2. Higher furnace temperatures lead to more complete decomposition of the oxalate.

3. Preheater temperature required to vaporize or sublime the oxalate depends on the pressure of the system.

For a large scale run, the oxalate was pyrolyzed at 660°, under a vacuum of 3.0-3.5 mm. The crude product was isolated by distillation to give 50% biallyl.

The configuration of substituted allyl radical during the course of a reaction is a topic of general interest in organic chemistry (93, 94, 95, 96). The possibility of interconversion of cis and trans radicals has been reported (97, 98). Since the generation of allyl radicals by oxalate pyrolysis in the gas phase is feasible, the investigation of the stereochemistry of allyl radicals and the positional isomer distribution arising from the coupling of allyl radicals were undertaken.

Table 12. Pyrolysis of diallyl oxalates at different conditions.

Furnace temp.	Head temp.	Vacuum	Product[a,b] % oxalate recovered	% biallyl	Total recovery
660°	65°	.07	24	40.5	64
660°	65°	.05-.1	23.5	43.4	66.8
660°	65°	0.7	18.4	43	61.4
660°	65°	2.5-2	16.7	66.4	83.1
660°	65°	3.5-3	16.1	69	85.1
660°	65°	aspirator vacuum			-c
660°	65°	10			-c
660°	65°	4			-c
570°	65°	10			-c
660°	80°	8	1.0	62.5	63.7
636°	70°	8	8.1	62.6	70.7
625°	80-85°	8	29	57.8	86.8
593°	70°	7.5-8	23	49.8	72.8
570°	80°	8	42	39.2	81
630°	65°	3.5	23.3	56	79.3

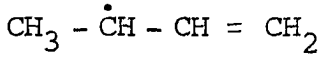
[a]Based on nmr analysis.

[b]Naphthalene as the internal standard.

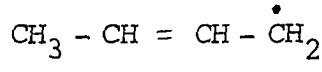
[c]The oxalate did not pass over the hot tube.

Pyrolysis of di-trans-crotyl oxalate

Glpc analysis of the pyrolysate of di-trans-crotyl oxalate at 535° gave a ratio of 2,6-octadiene/3-methyl-1,5-heptadiene equal to 52.4/47.6. Under the pyrolytic conditions only 6% of 3-methyl-1,5-heptadiene was converted to 2,6-octadiene. Thus the interconversion of these two dienes was considered negligible. A statistical coupling of the crotyl radicals in the forms XIII and XIV would give a ratio of 1 : 2 : 1 of 2,6-octadiene, 3-methyl-1,5-heptadiene

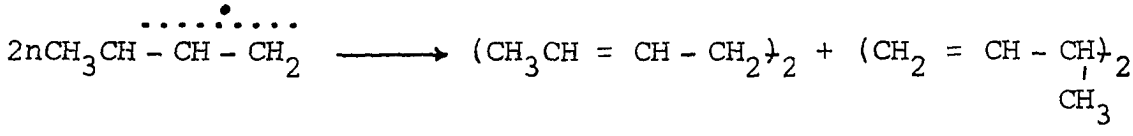


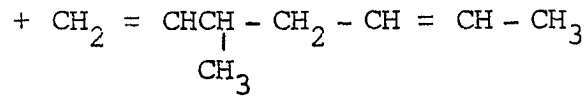
XIII



XIV

and 3,4-dimethyl-1,5-hexadiene. However due to the difference



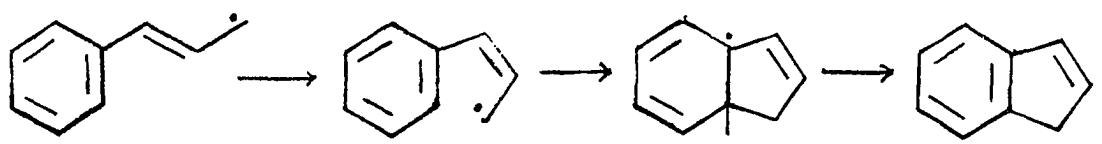


in stability of the products, one could expect to obtain more 2,6-octadiene than 3,4-dimethyl-1,5-hexadiene. This was observed in the case of Grignard reaction of 2-butenylmagnesium bromide (99, 100) (11% of 3,4-dimethyl-1,5-hexadiene, 34% of 3-methyl-1,5-heptadiene and 55% of 2,6-octadiene). 3,4-Dimethyl-1,5-hexadiene was obtained from the Grignard reaction

but not from oxalate pyrolysis (a high temperature process). Since it can undergo rearrangement to give the more stable 2,6-octadiene (81) at high temperature.

Pyrolysis of di-trans-cinnamyl oxalate

Relative amounts of the products obtained from the pyrolysis of di-trans-cinnamyl oxalate is shown in Table 13. Coupling products of the cinnamyl radicals were not obtained. Presumably if they formed, they can undergo decomposition at high temperature (82). The products obtained from the pyrolysis of di-trans-cinnamyl oxalate can be readily accounted for from the cinnamyl radicals generated. Intramolecular cyclization of the radical leads to indene and hydrogen abstraction gives allylbenzene and propenylbenzene.



XV XVI XVII XVIII

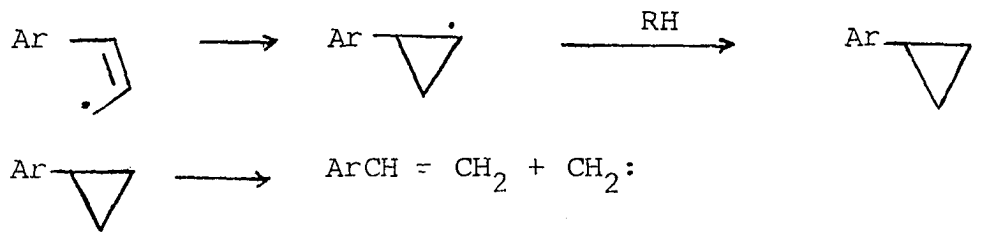
It is also possible that the intermediate radical XVII would disproportionate to give equal molar amounts of indene and indane. However, no indane was found. The formation of styrene is difficult to rationalize, certainly it was not formed from indene. Pyrolysis of indene under the same conditions gave only a trace of allylbenzene. It is possible that the intermediate cinnamyl radical may also form phenylcyclopropane. It might further undergo decomposition to give

Table 13. Relative number of moles of the products[a] obtained from the pyrolysis of di-trans-cinnamyl oxalate at 550° and 650°

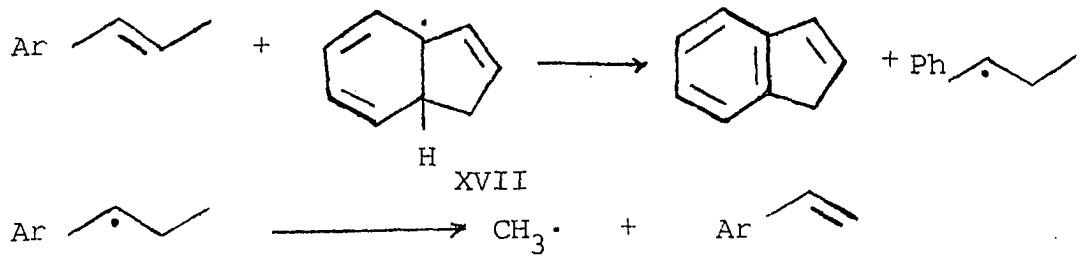
Temperature	Toluene	X	Styrene	Allylbenzene	X	cis-β-methylstyrene	trans-β-methylstyrene	Indene
550°	0.125	0.12	1.7	0.88	0.53	trace	1	7.4
650°	0.126	0.15	1.66	0.92	0.41	trace	1	6.1

[a]0.82 mole of indene was obtained from pyrolysis of cinnamyl formate at 650°; while 0.72 mole was obtained from pyrolysis of cinnamyl acetate at 650°.

styrene and methylene (101) under the pyrolytic conditions.



Another possibility is that the propenylbenzene undergoes hydrogen abstraction from the cyclic radical XVII to give the intermediate benzylic radical, which further undergoes β scission to give styrene and methyl radical.



It was also found that the yield of indene did not vary with pyrolysis temperature of the oxalate. Other unknown products formed are probably phenylcyclopropane, 1-phenylallene or α-methylstyrene.

Formation of indene from cinnamyl radical in our case is quite unusual and significant. No evidence for the formation of indene from cinnamyl radical has been given in the literature. Grignard reaction of cinnamyl chloride (102, 103) decomposition of acetyl peroxide in the presence of

allylbenzene (103) or thermal decomposition of t-butoxy cinnamyl perester (104) gave only dimer products and allylbenzene but no indene. In the latter two cases, it is quite likely that if indene formed, it would probably be attacked by the unstable alkoxy radicals present. Indeed substantial amount of polymeric material was reported in both cases.

Isotope effect of intramolecular cyclization of cinnamyl radical

Experimental evidence (77) has suggested that path 6 is the most reasonable mechanistic pathway for free radical substitution in aromatic systems. Mechanisms 4 and 5 are

$$R\cdot + ArH \longrightarrow RAr + H\cdot \qquad 4$$

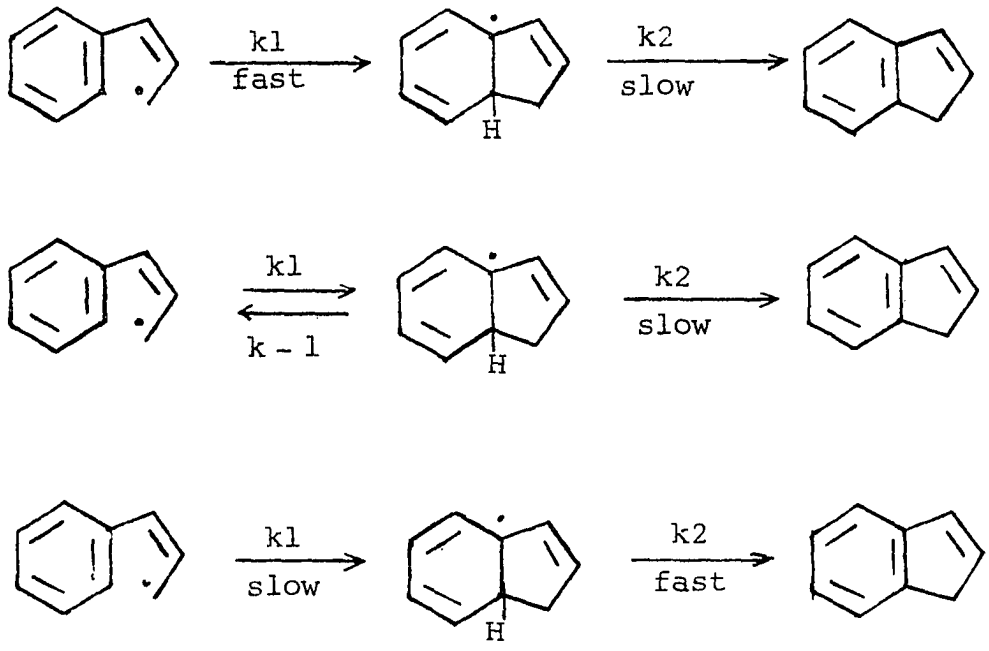
$$R\cdot + ArH \longrightarrow RH + Ar\cdot \xrightarrow{R\cdot} RH \qquad 5$$

$$R\cdot + ArH \longrightarrow \dot{R}ArH \xrightarrow{R\cdot} RAr + RH \qquad 6$$

considered unlikely on the basis of products obtained and the energies involved. As in any free radical aromatic substitution, a two-step mechanism (path 6) must also be operating in the cyclization of the cinnamyl radical to form

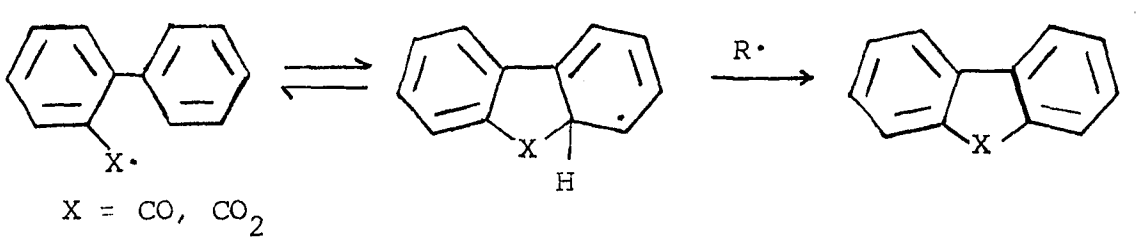
indene. The mechanism in which the intermediate radical XVII is converted to the product is not well understood. Loss of hydrogen atom from radical XVII is most likely by abstraction of organic material deposited on the pyrolysis column or a small amount of polymeric material present. The driving force for the hydrogen atom loss must be due to the formation of the conjugated system.

There are several mechanistic pathways which can be envisioned for the formation of indene from cinnamyl radical.



XVI XVII

Since the cinnamyl radical is relatively stable, it is quite likely that an equilibrium between XVI and XVII will occur prior to the hydrogen abstraction step. If the formation of the cyclic radical from the cinnamyl radical is reversible, with a rate faster than the hydrogen abstraction step, then one could expect an isotope effect for indene formation. Mass spectral analysis of a mixture of indene and 4-deuterioindene obtained from the pyrolysate of o-deuteriocinnamyl oxalate at 570° indicated an isotope effect, kH/kD of 2.94. This result indicated that the cyclic radical intermediate is in equilibrium with the cinnamyl radical and that a significant amount of carbon-hydrogen bond breakage occurred in the transition state. This result is in accord with that reported by Denney and Klemchuck (105). An isotope effect kH/kD of 1.38 at 143° was observed when fluorenone was formed from the reaction of 2-(o-deuteriophenyl)-benzaldehyde. Similarly, an isotope effect of 1.32 was also found for the decomposition of 2-(o-deuteriophenyl)benzoylperoxide to give the lactone of 2-carboxy-2'-hydrobiphenyl. They also concluded that an equilibrium exists between the starting material and the intermediate cyclic radical. The isotope effect they

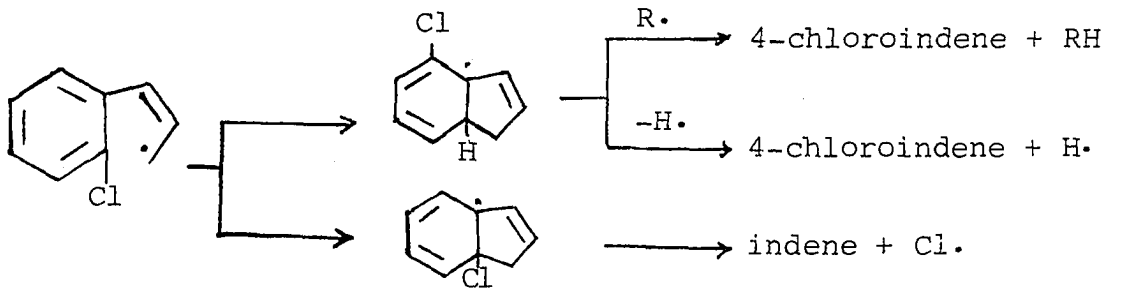


X = CO, CO_2

obtained is smaller than what we have obtained in this study.

Pyrolysis of di-trans-o-chlorocinnamyl oxalate

Glpc analysis of the pyrolysate of di-trans-o-chlorocinnamyl oxalate at 570° gave a ratio of 4-chloroindene/indene equal to 2.5. The last step of the formation of 4-



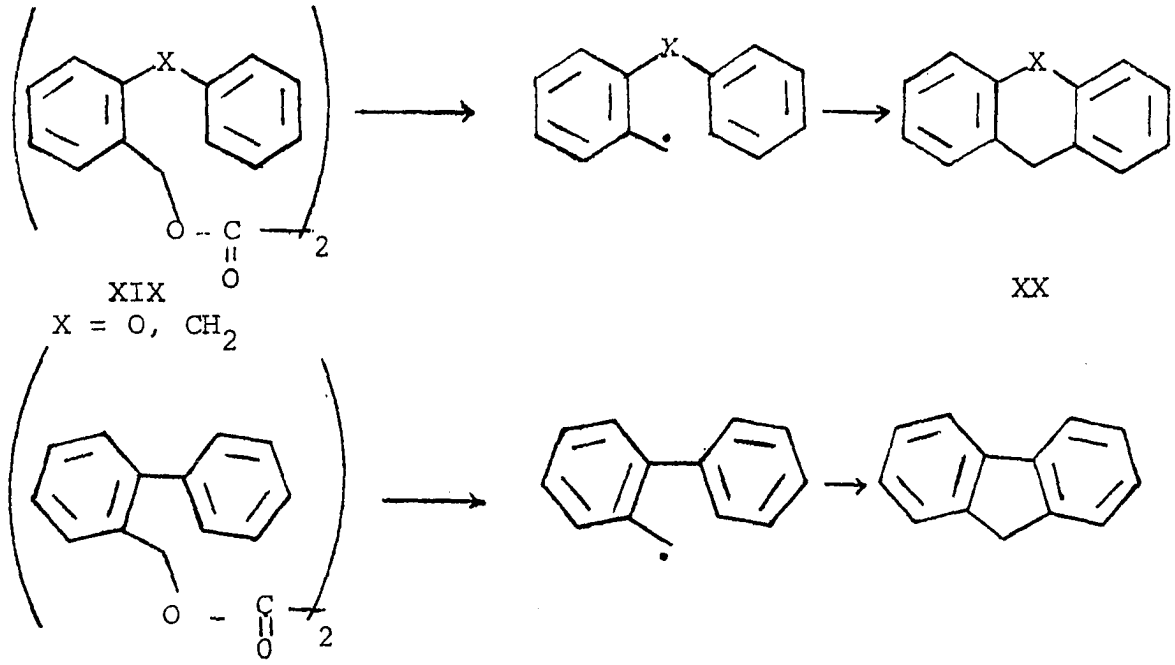
chloroindene and indene from the o-chlorocinnamyl radical may involve simply the breakage of the carbon-chlorine bond, carbon-hydrogen bond or atom abstraction by a radical species. The fact that more 4-chloroindene was obtained can be explained on the basis that the energy released from the formation of the R-H bond provides the driving force to break the carbon-hydrogen bond. Since the bond energy of a carbon-hydrogen bond (98.2 kcal/mole) is greater than that of a carbon-chlorine bond (78 kcal/mole), hydrogen atom abstraction will occur more readily than carbon-hydrogen bond breakage. While the formation of indene may occur primarily by carbon-chlorine bond breakage at the high temperature.

Aside from the bond energies involved, a steric effect due to the difference in size of a chlorine atom and hydrogen atom toward the approach of the radical species during the atom abstraction step certainly should be considered. Pyrolysis

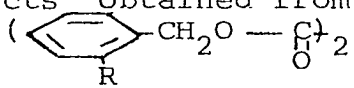
of other ortho-substituted cinnamyl oxalates might give better insights into the competitive formation of indenes.

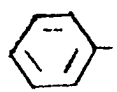
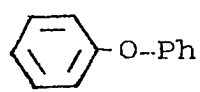
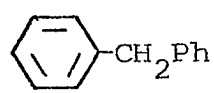
Pyrolysis of Di-o-phenylbenzyl Oxalate, Di-o-phenoxylbenzyl Oxalate and Di-o-benzylbenzyl Oxalate

The ready formation of indene from the cinnamyl radical is due primarily to the proximity of the ring. As an extension of the intramolecular radical cyclization, appropriate ortho substituted benzyl oxalates were pyrolyzed to give exclusively the desired cyclic compounds (Table 14).



Although many radical reactions are known which form new bonds between two atoms, only a few scattered examples exist in the literature concerning intramolecular radical cyclization (106-112). Formation of cyclic compounds from appropriate

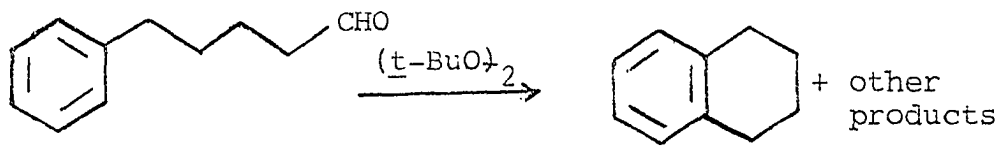
Table 14. Yields of products[a] obtained from pyrolysis of di-ortho-substituted benzyl oxalate ()$_2$

R	Products			
	fluorene[b]	1.44	o-phenyltoluene	0.05
	Xanthene	0.25	o-phenoxyltoluene	0.05
			a-phenoxylbenzyl alcohol	0.05
	9,10-dihydroanthracene	0.12	anthracene	0.12

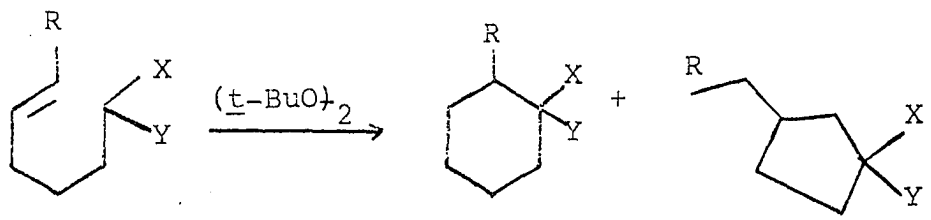
[a]Mole of product per mole of oxalate.

[b]0.6 mole of fluorene was obtained also from pyrolysis of methyl o-phenyl benzyl oxalate at 630°.

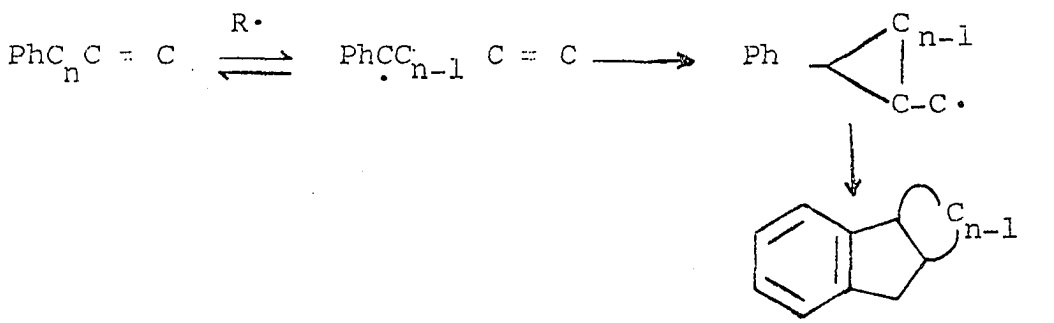
stable radicals showed also another synthetic utility of organic oxalate pyrolysis



(Ref. 106)



(Ref. 106)



(Ref. 112)

Pyrolysis of Dipropargyl Oxalate

A number of investigations has demonstrated the existence of the C_3H_3 radical. The nature of C_3H_3 is of considerable interest. In theory this radical can be represented as a resonance hybrid of propargylic structure XXI and allenic structure XXII. Both chemical and physical

$$H - C \equiv C - \dot{C}H_2 \longleftrightarrow H - \dot{C} = C = CH_2$$

XXI XXII

methods have been used to establish which structure resembles more closely the actual delocalized radical (113-118). Recently, it has been found (119) that bromopropargyl radical reacts at both termini during the equilibrium of propargyl bromide and bromoallene by hydrogen bromide. Several propargylic halides were reduced with tri-n-butyl tin hydride to give in each case a greater amount of acetylene than the isomeric allene (120). This result was explained on the basis of greater spin density at the propargylic end of the ambident C_3H_3 radical.

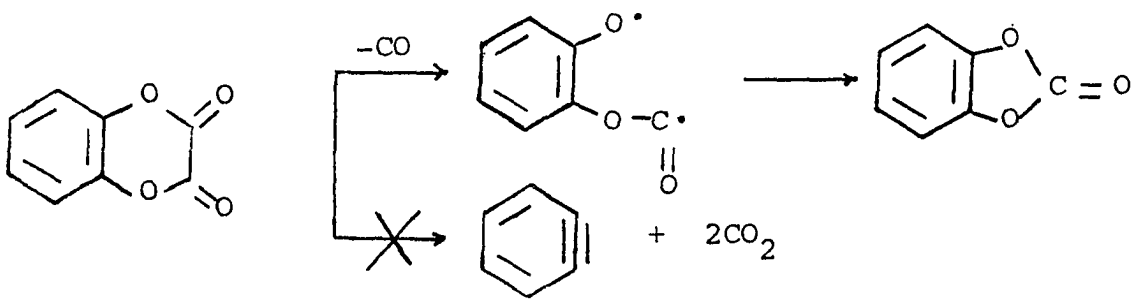
Pyrolysis of dipropargyl oxalate was then undertaken to generate propargylic radical. The relative reactivity of both forms of the ambident radicals could then be determined from the coupling products formed. By generating the substituted propargyl radicals, the effects of the radical structure on the product ratio can also be determined.

Benzene was the predominant product from the pyrolysis of dipropargyl oxalate at 600-660°. Nmr spectrum of the pyrolysate showed that complex products were obtained from other runs at lower temperature (350-500°) and high pressure (3mm-10mm). It has been reported (121, 122, 123) that pyrolysis of 1,5-hexadiyne gives different products under

different conditions. Benzene and fulvene have been obtained in one case at higher temperature. In our study presumably the propargyl radicals have been generated and have undergone coupling reactions. The 1,5-hexadiyne or the biallene formed then underwent further isomerization to give benzene and fulvene.

Pyrolysis of Catechol Oxalate

Pyrolysis of catechol oxalate in benzene solution over a hot column (550°) with nitrogen as a carrier gas gave exclusively catechol carbonate. The identity of this product was further confirmed by glpc peak enhancement and nmr spectrum comparison with an authentic sample. It is certain that a concerted bond breakage mechanism with the loss of two moles of carbon dioxide did not occur during the pyrolysis of the catechol oxalate. If it is, then the active intermediate benzyne could be trapped by benzene to give naphthalene and other products.



Several studies have reported that benzyne was generated by pyrolysis of appropriate compounds, cyclic phthaloyl peroxide (124), indanetrione (125, 126), benzodiazonium carboxylate (127), phthalic anhydride (128, 129) and chlorobenzene (130). The thermal fragmentation pattern of these compounds is usually parallel to that of electton impact in mass spectrometry (128); for example mass spectrum of phthalic anhydride showed peak at m/e = 76 (C_6H_4) with an intensity of 86% relative to the base peak. From the mass spectrum, it was shown that catechol oxalate fragmented only by stepwise loss of carbon monoxide and carbon dioxide. The driving force for the formation of the carbonate from catechol oxalate is probably due to the strength of phenyl-oxygen bond and the resulting stable planar carbonate ester formed.

The facile decomposition of catechol oxalate is no doubt a consequence of the weakness of the central carbon-carbon bond, the bond between two positively polarized carbon atoms. The diphenyloxalate, a linear oxalate analogous to catechol oxalate was quite stable. Only about 30% of the oxalate underwent decomposition at 650° to give the diphenylcarbonate. It is worth noting that the R moiety of the organic oxalates ($R-O-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-O-R$) having no β hydrogens indeed affects the mode of decomposition. When the R group is a stable radical, alkyl-oxygen bond cleavage occurs preferentially, if not, oxygen-carbonyl carbon bond cleavage occur exclusively as in the case of diphenyl oxalate.

EXPERIMENTAL

Equipment

1. Gas chromotographic analyses were conducted on an Aerograph Model 200 instrument.

2. Nuclear magnetic resonance spectra were taken on a Varian A-60 spectrometer with tetramethylsilane as an internal standard and deuteriochloroform as the solvent unless otherwise specified. Peak multiplicity is designated as singlet (s), doublet (d), triplet (t), quartet (q), quintet (qn) and multiplet (m).

3. Infrared spectra were taken on a Perkin Elmer Model 21 spectrophotometer and the characteristic frequencies are given in reciprocal centimeters (cm^{-1}).

4. Mass spectra were taken on an Atlas CH-4 spectrometer using an ionization potential of 70 eV unless otherwise specified.

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

6. Pyrolysis Apparatus. The pyrolysis apparatus consisted of a 2 x 30 cm Vycor tube packed with Vycor Rings and encased in a 30 cm electric furnace (Electric Apparatus Company). At one end of the tube was attached by a standard taper ground glass joint to a 2 x 4.5 cm tube closed at one end. This tube which held the starting material was encased

in a slightly larger test tube wrapped with heating tape. The other end of the pyrolysis tube was attached by means of a ball and socket joint to a U-shaped trap made from 38 cm of 1.2 cm Pyrex tubing with indentations. The trap was connected directly to a vacuum system. Temperature of the hot tube was monitored with an iron-constantan thermocouple connected to a Needs and Northrup potentiometer using an ice-water bath for the reference (Figure 1).

Chemicals

Table 15 lists the commercial sources for many of the chemicals used in this study.

Table 15. Chemicals and commercial sources

Chemical	Commercial source
Silica gel 100/200 mesh	Mallinckrodt
Oxalic acid dihydrate	J. T. Baker
Oxalyl chloride	Columbia, Eastman
Benzyl alcohol	Eastman
o-Nitrobenzyl alcohol	Eastman
o-Chlorobenzyl alcohol	Aldrich
p-Methoxybenzyl alcohol	Aldrich
α-Methylbenzyl alcohol	Aldrich

Table 15 (Continued)

Chemical	Commercial source
α-Ethylbenzyl alcohol	Aldrich
α-Isopropylbenzyl alcohol	Aldrich
Isobutyrophenone	Aldrich
Trifluoroacetophenone	Pierce
Perfluoropropionyl chloride	Pierce
Allyl alcohol	Aldrich
trans-Crotyl alcohol	Aldrich
Propargyl alcohol	Aldrich
1,6-Octadiene	Chemical Samples
3-Methyl-1,5-heptadiene	Aldrich
trans-Cinnamyl alcohol	Aldrich
trans-Cinnamyl formate	Aldrich
o-Dibromobenzene	Aldrich
o-Chlorobromobenzene	Aldrich
Acrolein	Eastman
Deuterium oxide (99.5% pure)	Columbia
o-Phenylbenzoic acid	Aldrich
o-Phenoxylbenzoic acid	K and K
o-Benzylbenzoic acid	K and K
Catechol	Eastman
Triethylamine (dried over Barium Oxide)	Matheson Coleman and Bell

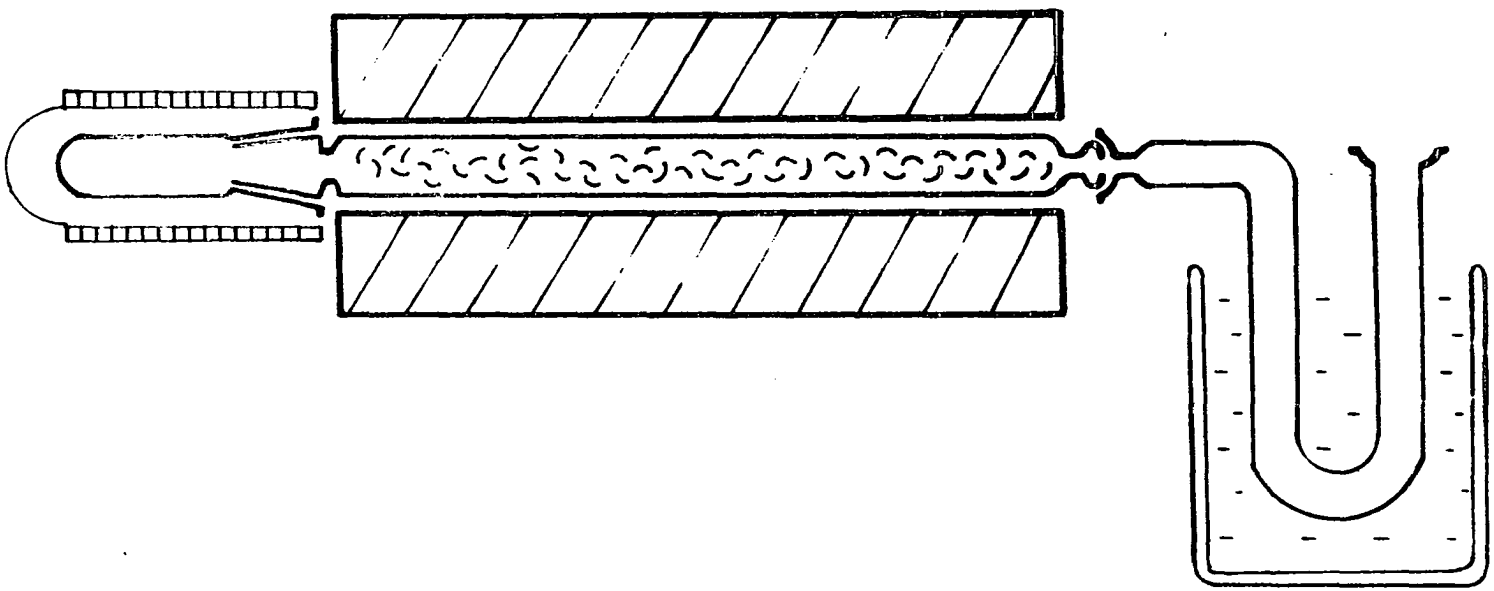


Figure 1. Gas phase pyrolysis apparatus

Preparation of Benzyl Alcohols

p-Chlorobenzyl alcohol, m-chlorobenzyl alcohol and α-naphthyl methanol

These were prepared from their respective chlorides (obtained from Aldrich Chemical Company) by a method similar to Hartman and Rahrs (131).

p-Bromobenzyl alcohol

This alcohol was prepared from p-bromobenzyl bromide (obtained from Aldrich Chemical Company) by a method similar to that of Hartman and Rahrs (131).

p-Methylbenzyl alcohol

This alcohol was obtained from p-methylbenzyl acetate (obtained from Columbia Chemical Company) by a method similar to that of Hartman and Rahrs (131).

p-Cyanobenzyl alcohol

This alcohol was prepared from its chloride (obtained from K and K Chemical Company) by a method similar to that of Hartman and Rahrs (131). Benzyl alcohol-α-d_2 was obtained from Prof. G. A. Russell.

α-Trifluoromethylbenzyl alcohol

α-Trifluoromethyl benzyl alcohol was prepared by lithium aluminium hydride reduction of trifluoroacetophenone.

A yield of 80% was obtained, bp 70-74°/15mm (lit. 132) bp 64-65°/5mm). Nmr spectrum showed peaks at δ, 7.32 (s, 5H), 3.33 (q, 1H), 4.82 (q, 1H).

α-Perfluoroethylbenzyl alcohol

α-Perfluoroethylbenzyl alcohol was prepared by the reduction of perfluoropropionylphenone with lithium aluminium hydride in 80% yield, bp 45-50°/2.8mm (lit. (132) bp 52°/3mm). Nmr spectrum showed peaks at δ, 7.35 (s, 5H), 5.04 (2 doublets, J = 8cps, 1H) and 4.26 (s, 1H).

α-t-Butylbenzyl alcohol

α-t-Butylbenzyl alcohol was prepared according to the method of Conant and Blatt in 40% yield, bp 74-76/2mm (lit. (132) bp 121.7-123°/2mm). Nmr spectrum showed peaks at δ 7.2 (s, 5H), 4.22 (s, 1H) and 0.85 (s, 1H).

1-(o-Deuteriophenyl)propen-1-ol

1-(o-Deuteriophenyl)propen-1-ol was prepared according to the method of Ouellete et al. (134) with modification.

o-Deuteriophenylmagnesium bromide was prepared by adding o-deuteriobromobenzene, 1.5 gm (.009 mole) from a dropping funnel to a suspension of magnesium turnings 0.7 gm (.029) mole) in 40 ml of anhydrous ether in a three-neck flask fitted with stirrer and reflux condenser. A trace of iodine was added to insure rapid initiation of the reaction.

The remaining 1.5 gm (.015 mole) of bromobenzene was then added dropwise in 20 minutes. Half an hour later, 2.2 ml of acrolein in 10 ml of anhydrous ether was added dropwise. After an hour, 20 ml of 20% aqueous ammonium chloride was added. The reaction mixture was stirred for another 30 minutes. The ether layer was separated and the aqueous layer was extracted with ether (2 x 50 ml). The ether extract was dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was then vacuum distilled to give colorless liquid, bp 80-85°/8mm (lit. (134) bp 76-76/0.18mm) in 55% yield.

1-(o-Chlorophenyl)propen-1-ol

This alcohol was prepared by the method described for the preparation of 1-(o-deuteriophenyl)propen-1-ol from o-chlorophenylmagnesium bromide and acrolein in 58% yield, bp 81-82°/0.4mm. Nmr spectrum showed peaks at δ 7.3 (m, 4H), 5-6.3 (complex multiplet, 4H) and 3.16 (s, 1H).

o-Phenylbenzyl alcohol

A solution of o-phenylbenzoic acid, 7.27 gm (0.037 mole) in 50 ml of anhydrous ether was added dropwise to a stirred mixture of 1.57 gm (0.041 mole) lithium aluminium hydride and 120 ml of anhydrous ether in a 500 ml two-neck flask. Addition required 2 1/2 hours. The milky solution

was stirred further for another hour. A solution of 4 ml of concentrated sulfuric acid in 10 ml of water was then carefully added. The resulting mixture was then stirred until homogeneous. The ethereal layer was separated. The water layer was further extracted with ether (2 x 100 ml). The ether extract was then washed with saturated sodium bicarbonate solution, dried over magnesium sulfate and filtered. Concentration of the ethereal solution gave an oil. This crude product was used directly for oxalate preparation. Nmr spectrum showed peaks at δ, 7.25 (m, 9H), 4.5 (s, 2H) and 3.65 (s, 1H).

o-Phenoxybenzyl alcohol

o-Phenoxylbenzoic acid was reduced by lithium aluminium hydride to the corresponding alcohol as previously described for the preparation of o-phenylbenzyl alcohol. Nmr spectrum showed peaks at δ, 7.12 (m, 9H), 4.65 (s, 2H) and 2.81 (s, 1H).

o-Benzylbenzyl alcohol

This alcohol was prepared by lithium aluminium hydride reduction of the corresponding acid as described above for the preparation of o-phenylbenzyl alcohol. Nmr spectrum showed peaks at δ, 7.11 (m, 9H), 4.48 (s, 2H), 3.95 (s, 2H) and 3.18 (s, 1H).

Preparation of Intermediates

Benzylchloroglyoxalate

It was prepared by a method similar to that of Rhoads and Mischels (135).

2,3-Diphenylbutanes

These diastereomers were prepared according to the method of Barber et al. (55) through a Grignard coupling reaction of α-chloroethylbenzene which was in turn prepared as described by Shirley (136).

Perfluoropropionylphenone

This ketone was prepared according to the method of Simmons et al. (137) by the Friedel Craft's reaction of perfluoropropionyl chloride with benzene in the presence of aluminium chloride in a yield of 30%, bp 159-161° (lit. (137) bp 161-162°).

Methyl oxalyl chloride

It was prepared by D. Zabel (25).

o-Deuteriobromobenzene

o-Dibromobenzene, 25 gm (0.102 mole) was added slowly to a suspension of magnesium turnings, 3.0 gm (0.122 mole) in 50 ml of anhydrous ether in a three-neck flask fitted with a reflux condenser (connected to a drying tube) and a

stirrer. Addition required 30 minutes. Deuterium oxide (20 ml) was then added 30 minutes later. The reaction mixture was stirred for another half hour. The ether layer was then separated and the aqueous layer was further extracted with ether (2 x 20 ml). The ethereal extract was dried over anhydrous magnesium sulfate and then concentrated on a rotary evaporator to give a light yellow liquid. The crude product was then distilled to give a colorless liquid, bp 155-158° (lit. (138) 155-157°). The product is further confirmed by VPC peak enhancement with bromobenzene.

Preparation of Esters

Preparation of symmetrical oxalates

Method I is patterned after that of Lespagnol (139). This method involves the reaction of the alcohol with anhydrous oxalic acid catalyzed by a trace of sulfuric acid.

Method II is illustrated by the preparation of di-p-bromobenzyl oxalate. A quantity of 0.9 ml (0.0103 mole) of oxalyl chloride was added slowly to an ice-cooled stirred solution of p-bromobenzyl alcohol, 3.74 gm (0.02 mole) and triethylamine, 4 ml (0.03 mole) in 100 ml of anhydrous ether. Ten minutes later the reaction mixture was filtered. The precipitate was washed with water and recrystallized from 95% ethanol to give 3.2 gm (75%) of white leaflets.

Method III is similar to method II, except the work up procedure is different. The reaction mixture was extracted with water. The ethereal solution was then combined and concentrated on a rotary evaporator to give the crude compound. Recrystallization of the crude product from suitable solvent gave the pure oxalate.

In Tables 16, 17, 18 and 19 are presented pertinent data for the dibenzyl, diallyl and di-α-alkylbenzyl oxalates.

Benzyl p-chlorobenzyl oxalate

Benzyl chloroglyoxalate 2.22 gm (1.12 m mole) was added dropwise to a stirred solution of p-chlorobenzyl alcohol, 1.60 gm (1.12 m mole) and triethylamine (2 ml) in anhydrous ether (100 ml). When addition was complete the reaction mixture was stirred for 10 minutes. The reaction mixture was then filtered and washed thoroughly with ether. The filtrate was evaporated on a rotary evaporator to give a white crystalline solid. Recrystallization of the crude product from 95% ethanol gave a 42% yield of white crystals, mp 96-98°.

Ir spectrum showed C = O stretching frequencies at 1745 and 1770 cm^{-1}.

Nmr spectrum showed peaks at δ, 7.25 (s, 9H), 5.28 (s, 2H) and 5.22 (s, 2H).

Anal. Calcd for $C_{16}H_{14}O_4Cl$:: C, 63.00; H, 4.39;

Table 16. Method of preparation, yields, melting points, boiling points and elemental analyses of dibenzyl and diallyl oxalates $(RCH_2\text{-}O\text{-}CO)_2$

R	Method of Prep'n	Yield	Melting point[a] or boiling point °C	Elemental analyses, %[b]					
				Found			Calculated		
				C	H	other	C	H	other
C_6H_5	I	92%	79-80[c]						
p-ClC_6H_4	I	86%	118.5-120	56.67	3.56	21.02(Cl)	56.66	3.57	20.91(Cl)
o-ClC_6H_4	I	71%	77-79	56.57	3.56	20.90(Cl)	56.66	3.57	20.91(Cl)
m-ClC_6H_4	I	88%	104-106	56.59	3.59	20.71(Cl)	56.66	3.57	20.91(Cl)
p-BrC_6H_4	II	75%	136-138	44.78	2.88	37.35(Br)	44.87	2.83	37.35(Br)
p-FC_6H_4	I	58%	107-109	62.96[d]	3.96[d]	--	62.73	3.95	12.41(F)

[a]Recrystallized from 95% ethanol unless otherwise specified.

[b]Analyses by Spang Microanalytical Laboratory unless otherwise specified.

[c]Lit. (120) mp 79-80°.

[d]Analyses by M-H-W Laboratories.

Table 16 (Continued)

R	Method of Prep'n	Yield	Melting point[a] or boiling point °C	Elemental analyses, %[b]					
				Found			Calculated		
				C	H	other	C	H	other
p-$CH_3C_6H_4$	I	54%	99-100	72.26	6.15	--	72.43	6.09	--
p-NCC_6H_4	II	41%	194-197[e]	67.32	3.80	8.71(N)	67.48	3.77	8.75(N)
α-Naphthyl	II	58%	104-106	77.47[d]	4.92[d]	--	77.81	4.90	--
m-$O_2NC_6H_4$	I	88%	133-135[f]	53.53	3.37	7.65(N)	53.32	3.36	7.77(N)
p-$CH_3OC_6H_4$	II[g]	64%	133-114.5	65.41	5.39	--	65.43	5.49	--
o-phenylC_6H_4	III	73%	108-110	79.55	5.22	--	79.59	5.25	--

[e]Recrystallized from hot dichloromethane.

[f]Recrystallized from hot benzene.

[g]No triethylamine was used.

Table 16 (Continued)

R	Method of Prep'n	Yield	Melting point[a] or boiling point °C	Elemental analyses, %[b]					
				Found			Calculated		
				C	H	other	C	H	other
o-phenoxyl C_6H_4	III	45%	94-96	74.02	4.86	--	73.98	4.88	--
o-benzyl C_6H_4	III	55%	117-119[h]	79.80	5.78	--	79.91	5.82	--
trans- $C_6H_5CH=CH$	II	70%	102-104	74.51	5.44	--	74.50	5.63	--
trans- o-ClC_6H_5-CH=CH	III[i]	50%	98-100	60.96	4.06	18.50	61.38	4.12	18.13
trans- $CH_3CH=CH$	I	82%	bp 100-102/2mm	60.51	6.98	--	60.57	7.12	--
$CH_2=CH$	I	75%	bp 215-216[j]						

[h]Recrystallized from chloroform-hexane mixture.

[i]Di-1-(o-chlorophenyl)propenyl oxalate was prepared which underwent allylic isomerization.

[j]Lit. (139) bp 215°.

Table 17. Nmr signals and ir absorption bands of dibenzyl and diallyl oxalates $(RCH_2O\text{-}CO)_2$

R	Chemical shifts, δ[a]			IR frequency, cm^{-1}[b]	
	Aromatic H	CH_2	other	C=O	other
C_6H_5	7.28(s)	5.28(s)		1780,1740	
p-ClC_6H_4	7.30(s)	5.22(s)		1770,1745	
o-ClC_6H_4	7.27-7.66(m)	5.42(s)		1770.1755	
m-ClC_6H_4	7.46-7.22(m)	5.26(s)		1780,1743	
p-BrC_6H_4	7.38(q)	5.24(s)		1768,1740	
p-FC_6H_4	6.88-7.55(m)	5.25(s)		1770,1740	
p-$CH_3C_6H_4$	7.04-7.36(m)	5.12(s)	2.31(s)(CH_3)	1770,1742 1770[c]	
p-NCC_6H_4	-d			1755[c]	2240(CN)
α-Naphthyl	7.25-8.1(m)	5.75(s)		1770,1740	

[a] Deuteriochloroform was used as solvent unless otherwise specified.

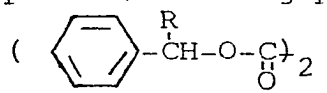
[b] Chloroform was used as solvent unless otherwise specified.

[c] A KBr pellet was used.

[d] Insoluble in common spectral solvents.

Table 17 (Continued)

R	Chemical shifts, δ[a]			IR frequency, cm^{-1}[b]	
	Aromatic H	CH_2	other	C=O	other
m-$O_2NC_6H_4$	-[d]			1745[c]	
p-$CH_3OC_6H_4$	7.4-6.78(q)	5.2(s)	3.78(s)(OCH_3)	1760,1740	
o-phenylC_6H_4	7.31(s)	5.2(s)		1775,1752	
o-phenoxylC_6H_4	7.15(m)	5.41(s)		1770,1740	
o-benzylC_6H_4	7.2(m)	5.22(s)	4.05(s)(CH_2)	1770,1740	
trans-C_6H_5-CH=CH	7.27(m)	4.88 (d,J=6cps)	6.4(m)(CH=CH)	1770,1740	
trans o-ClC_6H_5-CH=CH	7.05-7.7(m)	4.98 (d,J=8cps)	6.08-6.54(m)	1770,1740	
trans-CH_3CH=CH		4.81 (d,J=5.5cps)	5.25-6.22(m)(CH=CH) 1.72(d,J=5.5cps)(CH_3)	1770,1740	
CH_2=CH		4.7 (d,J=6cps)	6.38-5.23(m)(CH=CH)	1775,1740	

Table 18. Method of preparation, yields, melting points, boiling points elemental analyses of di-α-alkyl benzyl oxalates 

R	Method of Prep'n	Yield	Melting point or boiling point	Elemental analyses			
				Found		Calculated	
				C	H	C	H
CH_3	III	65	bp 172-6/1.5mm	71.79	5.98[a]	72.45	6.09
CH_2CH_3	III	56	bp 170-2/0.4mm	73.67	6.92[b]	73.58	6.79
$CH(CH_3)_2$	III	68	bp 160-3/.2mm	74.46	7.43[a]	74.53	7.40
CF_3	III	45	mp 97-99	52.80	2.87[b]	53.18	2.98
CF_2CF_3	III	60[c]	-d	47.28	2.58	47.42	2.39

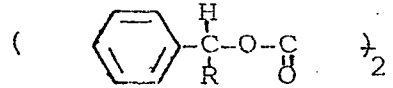
[a]Analyzed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

[b]Analyzed by MHW Laboratories, Garden City, Michigan.

[c]Estimated approximately from nmr spectrum.

[d]No pure product was isolated. The analytical sample was collected by glpc.

Table 19. NMR signals and ir absorption bands of di-α-alkyl benzyl oxalates



R	Chemical shifts aromatic H	CH	other	IR frequency cm^{-1} C = O
$-CH_3$	7.3(m)	5.96(q)	1.57(d,J=7cps)(CH_3)	1770,1740
$-CH_2CH_3$	7.3(m)	5.78(t,J=7cps)	1.83(qn)(CH_2) 0.88(t,J=7cps)(CH_3)	1775,1730
$-CH(CH_3)_2$	7.3(s)	5.61(d,J=7cps)	2.21(m)(CH) 1.0(d,J=7cps)(CH_3) 0.82(d,J=7cps)(CH_3)	1770,1740
$-CH(CF_3)$	6.22(s)	4.86(q)		1795,1770
$-CH(CF_2CF_3)$	7.45(s)	6.3(q)		1790,1770

Cl, 11.62. Found: C, 63.08; H, 4.46; Cl, 11.36.

Benzyl benzyl-α,α-$\underline{d}_2$ oxalate

Benzyl benzyl-α,α-$\underline{d}_2$ oxalate was prepared from benzyl chloroglyoxylate and benzyl alcohol-α-$\underline{d}_2$ by the same method used to prepare benzyl p-chlorobenzyl oxalate. Recrystallization of the crude product from 95% ethanol gave 76% yield of white crystals, mp 79-80°.

Ir spectrum showed C = O stretching frequencies at 1740 and 1770 cm^{-1}.

Mass spectral analysis of the thrice recrystallized oxalate showed that it was 8.3% $\underline{d}_o$, 21.6% $\underline{d}_1$ and 70.1% $\underline{d}_2$. Pertinent mass spectral data are presented in Table 20. In agreement with the mass spectral data an nmr spectrum of the oxalate showed that 20% of the benzylmethylene hydrogens are protons.

Di-α,α-dimethylbenzyl oxalate

This oxalate was prepared by the method described previously (23) in 91% yield, mp 68-70°.(recrystallized from 95% ethanol). Ir spectrum showed C = O stretching frequencies at 1740 and 1772 cm^{-1}. Nmr spectrum showed peaks at δ, 7.32 (s, 5H) and 1.85 (s, 6H).

Anal Calcd for $C_{20}H_{22}O_4$: C, 73.58; H, 6.80. Found: C, 73.12; H, 6.85.

Table 20. Mass spectral data for natural and deuterated dibenzyl oxalate.

	m/e	Intensity of natural sample[a]	Intensity of deuterated sample[b]	Calc'd peaks for d_o	Calc'd peaks for d_1	Calc'd peaks for d_2
P	270	100	2.5	2.5	--	--
P+1	271	19.8	7	0.50	6.5	--
P+2	272	3.36	22.5	0.084	1.29	21.13

[a]Ionization voltage was 70 ev.

[b]Ionization voltage was 23 ev.

Di-3-(o-deuteriophenyl)-propenyl oxalate and di-(o-deuteriophenyl)-propenyl oxalate

The di-1-(o-deuteriophenyl)-propenyl oxalate was prepared by method III. The nmr spectrum of the crude product showed peaks at δ, 7.35 (s, 4.1H), 5.85 - 6.4 (m, 2H) and 5.15 - 5.55 (m, 2H) which are characteristics of this structure. Upon standing for a few days, the crude product solidified. Recrystallization of the crude product from 95% ethanol gave 55% yield of white crystals. The mp, 102-104°, corresponded to that of di-trans-cinnamyl oxalate (di-3-(o-deuteriophenyl)-propenyl oxalate was actually the isomerized product). Mass spectral analysis of the twice

recrystallized oxalate showed that it was 1.37% $\underline{d}_0$, 15.68% $\underline{d}_1$ and 82.95% $\underline{d}_2$. Pertinent mass spectral data are presented in Table 21. Nmr spectrum also indicated that at least 92% of the ring hydrogens are protons.

Table 21. Mass spectral data for natural and deuterated di-trans-cinnamyl oxalate

	m/e	Intensity of natural sample	Intensity of deuterated sample	Calc'd peak for $\underline{d}_0$	Calc'd peak for $\underline{d}_1$	Calc'd peak for $\underline{d}_2$
P	322	100	0.3	0.3	--	--
P+1	323	23.5	3.5	0.071	3.43	--
P+2	324	41.2	19.0	0.0124	0.811	18.18

Methyl o-phenylbenzyl oxalate

Methyl oxalyl chloride, 1.5 gm (.0123 mole) was added dropwise to a stirred solution of o-phenylbenzyl alcohol 2.27 gm (.0123 mole), triethylamine 1.6 ml and 20 ml of anhydrous ether. Addition took place for 10 minutes. The reaction mixture was stirred for one more hour. Water (100 ml) was then added and the reaction mixture was extracted with ether (3 x 20 ml). The ethereal solution was dried over magnesium sulfate and concentrated on a rotary

evaporator to give an oil. Recrystallization of the crude product from 95% ethanol gave fine needles in 65% yield, mp 106-108°. Ir spectrum showed C = 0 stretching frequencies at 1740 and 1770 cm^{-1}. Nmr spectrum showed peaks at δ 7.3 (m, 9H), 5.6 (s, 2H) and 3.72 (s, 3H).

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.08; H, 5.23. Found: C, 79.17; H, 5.29.

Di-propargyl oxalate

Di-propargyl oxalate was prepared by the method of Lespagnol (139). The crude product obtained was recrystallized from hot 95% ethanol to give white prism in 20% yield, mp 96-97° (lit. (139) mp 97-98°).

Ir spectrum showed C = 0 stretching frequencies at 1755 and 1788 cm^{-1} and C-H stretching at 3340 cm^{-1}. Nmr spectrum showed peaks at δ, 4.87 (d, 2H) and 2.56 (t, 4H).

Catechol oxalate

Catechol 3 gm (0.0273 mole) and oxalyl chloride 3.44 gm (0.0273 mole) were dissolved in 50 ml of anhydrous ether in a 50 ml flask fitted with reflux condenser, which was in turn fitted to a drying tube. Then sodium, 1.7 gm (0.074 mole) was added carefully into the ethereal solution. The reaction mixture was stirred at room temperature for 21 hours. The ether layer was then separated. The residue was extracted with ether (2 x 80 ml) and finally with benzene (3 x 80 ml).

The unreacted sodium was then destroyed by adding anhydrous methanol gradually to the flask. Both the ether and benzene extracts were concentrated on a rotary evaporator to give white solids. Recrystallization of the crude product from benzene gave 1.03 gm (25%) of white needles, mp 184-186°, (lit (140) mp 185°). *Ir spectrum (Nujol or KBr) showed* C = O stretching frequencies at 1772 and 1810 cm^{-1}. Nmr spectrum (acetone) showed a sharp singlet at 2.69 δ. UV spectrum in 95% ethanol showed maximum at 275 mμ ($\varepsilon = 2.69 \times 10^3$) and 215 mμ ($\varepsilon = 6.07 \times 10^4$).

The mass spectrum of catechol oxalate showed the following ion fragments and their relative intensities.

m/e		m/e	
164	62.1%	63	46 %
132	43.6%	62	8.6%
92	67.8%	61	2.3%
80	6.3%	54	2.3%
76	4.6%	53	3.5%
68	6.9%	52	18.4%
65	6.9%	50	13.8%
64	100 %	40	4.6%

α-t-Butylbenzyl acetate

α-t-Butylbenzyl acetate was prepared according to the method of S. Winstein, bp 84-86°/2.8 mm (lit. (141) bp 80-80.2°/2 mm) in 77% yield. Nmr spectrum showed peaks at δ,

7.26 (s, 5H), 5.51 (s, 1H) 2.02 (s, 1H) and 0.95 (s, 9H).

trans-Cinnamyl acetate

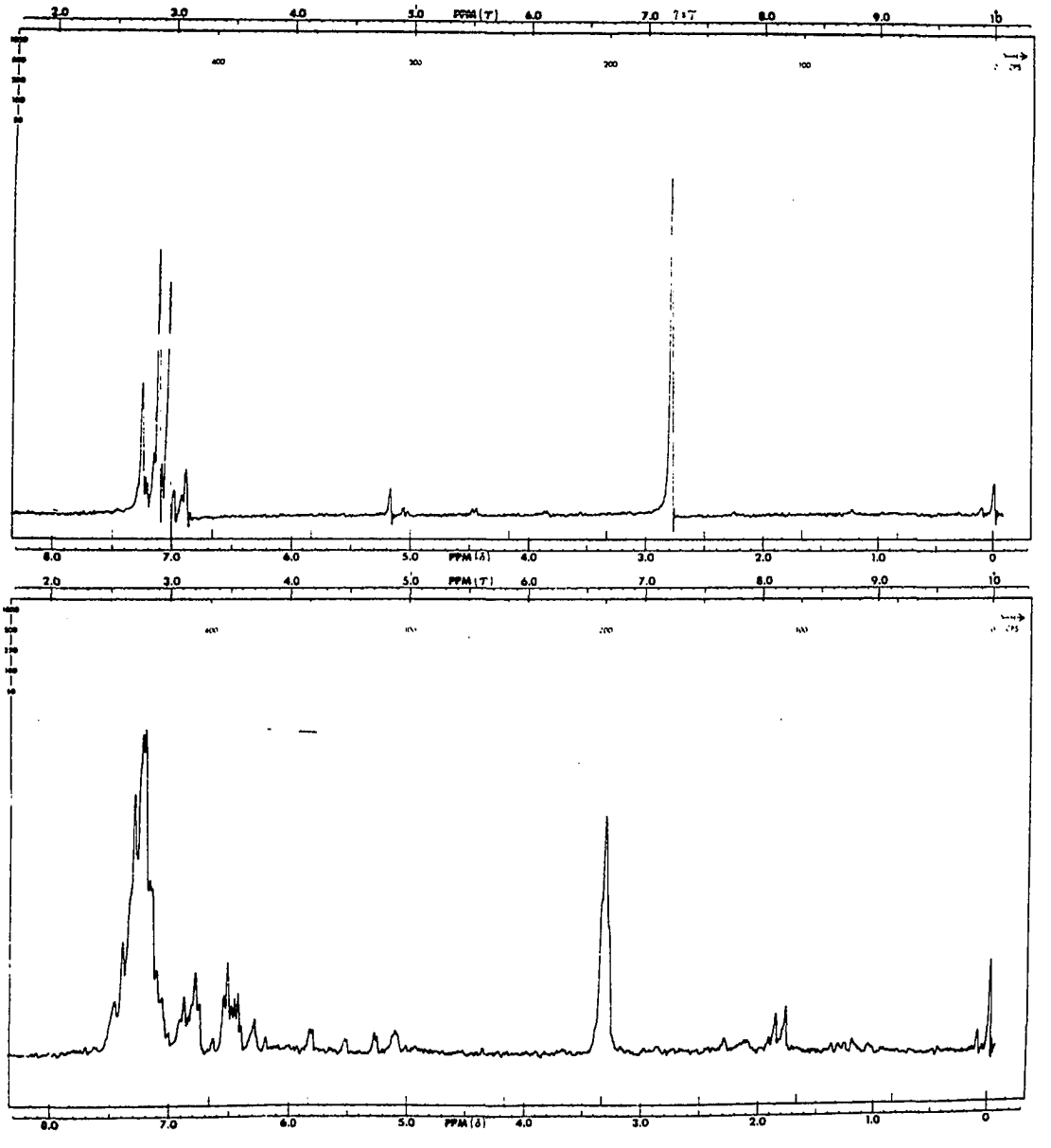
Acetyl chloride, 8.9 gm (0.114 mole) was added dropwise to a stirred solution of trans-cinnamyl alcohol, 15.27 gm (0.114 mole) and triethylamine, 16 ml (0.114 mole) in 100 ml of anhydrous ether in a two neck flask equipped with a dropping funnel and a reflux condenser fitted with drying tube. Addition took 30 minutes. The reaction mixture was then stirred at room temperature for another 12 hours. Water (150 ml) was then added to the reaction mixture. The ethereal layer was separated and the water layer was further extracted with ether (2 x 100 ml). The ether extract was dried over magnesium sulfate, filtered and concentrated under reduced pressure to give an oil. The crude product was distilled to give yellow liquid, bp 117-120°/11 mm (lit. (142) bp 141°/18 mm) in 68% yield.

Pyrolysis of Oxalates and Other Esters

The procedure for the pyrolysis of oxalate at high temperature under vacuum is illustrated by that of dibenzyl oxalate, unless otherwise specified. The vacuum used for pyrolysis was usually .05 - .1 mm, unless otherwise noted. Figure 2 and 3 showed the nmr spectra of the pyrolysate of di-p-chlorobenzyl oxalate and di-trans-cinnamyl oxalate.

Figure 2. Pyrolysate of di-p-chlorobenzyl oxalate

Figure 3. Pyrolysate of di-trans-cinnamyl oxalate


PPM (τ)
PPM (δ)

Pyrolysis of dibenzyl oxalate

A quantity of 1 gm (3.7 mmol) of dibenzyl oxalate in an aluminium foil pan was placed in the head of the apparatus and the system was evacuated to 0.05 mm. The cold trap was cooled with liquid nitrogen, the furnace was heated to 660° and the head was heated to 115-125°. Over a period of 2 hours all of the oxalate had sublimed. The liquid nitrogen trap was removed and the system was opened to the atmosphere. The crude pyrolysate was washed out of the trap with the use of a small amount of pentane and then acetone. The solvent was evaporated, an nmr spectrum of the pyrolysate was taken and peaks at δ 2.32 (toluene), 2.82 (bibenzyl), 4.48 (benzyl alcohol), 4.50 (benzyl ether), 5.22 (dibenzyl oxalate) and 10.0 (benzaldehyde) were integrated. The assignment of these peaks was confirmed by nmr spectra of authentic samples. At least 90% of these products were bibenzyl.

Recrystallization from 95% ethanol of the bibenzyl obtained from chromatography of the pyrolysate on a silica gel column using pentane as the eluent gave 0.396 gm (2.18 mmol) of bibenzyl, 59% yield, mp 51-52° (lit. (32) mp 51.5-52.5°).

Yields and melting points of bibenzyls that were prepared by pyrolysis are given in Table 2. The ir spectrum of p,p'-dicyanobibenzyl showed no carbonyl absorptions, and its mass spectrum showed a molecular ion peak of m/e 232.

Pyrolysis of benzyl p-chlorobenzyl oxalate

Pyrolysis of this dibenzyl oxalate was carried out in the usual manner. Glpc analysis of the pyrolysate on a 20% SE 30 column (7' x 1/4") showed three main peaks in the ratio of 1.00 : 2.04 : 1.00. The first and last peaks were identified as bibenzyl and p,p'-dichlorobibenzyl by peak enhancement with authentic samples. The product giving rise to the second glpc peak was collected and identified as p-chlorobibenzyl by its melting point, 47-49°, (lit. (143) mp 49°) and consistent nmr spectrum with appropriate proton integration ratio. Since the relative thermal conductivity of bibenzyl to p,p'-dichlorobibenzyl was found to be 1 : 1.03, the relative thermal conductivities used for the three peaks were 1 : 1 : 1.

Thermal stability of p-chlorobibenzyl

The thermal stability of p-chlorobibenzyl under the pyrolytic condition was established by passing 10 mg quantities of p-chlorobibenzyl (collected by glpc from the pyrolysate of benzyl p-chlorobenzyl oxalate) through the pyrolysis tube heated to 650° with a head temperature of 75-125°. Glpc analysis of the pyrolysate from two runs showed the presence of 12.2 ± 1.6% bibenzyl, 76.0 ± 2.6% p-chlorobibenzyl and 11.8 ± 1.0% p,p'-dichlorobibenzyl.

Pyrolysis of benzyl benzyl-α-α-$\underline{d}_2$ oxalate

The recrystallized bibenzyl obtained from column chromatography of the pyrolysate was submitted to mass spectral analysis. In Table 22 are presented pertinent mass spectral data from which percentages of $\underline{d}_0$ - $\underline{d}_4$ species were calculated and presented in Table 3.

The percentage of $\underline{d}_0$ - $\underline{d}_4$ species of the bibenzyl obtained from an intermolecular process were then calculated. The benzyl oxalate contained 8.3% $\underline{d}_0$, 21.6% $\underline{d}_1$ and 70.1% $\underline{d}_2$. Therefore 54.15% of the benzylic hydrogens were $\underline{d}_0$, 10.8% were $\underline{d}_1$ and 35.05% were $\underline{d}_2$.

The probabilities of forming bibenzyls-$\underline{d}_0$-$\underline{d}_4$ are as follows:

$\underline{d}_0$ = (0.5415)(0.5415) = 0.293

$\underline{d}_1$ = (0.5415)(0.108) + (0.108)(0.5415) = 0.117

$\underline{d}_2$ = (0.5415)(0.3505) + (0.3505)(0.5415) + (0.108)(0.108)
= 0.391

$\underline{d}_3$ = (0.108)(0.3505) + (0.3505)(0.108) = 0.759

$\underline{d}_4$ = (0.3505)(0.3505) = 0.123

Multiplying the above probabilities by 100 give the calculated percentages for an intermolecular process.

Pyrolysis of di-α-methylbenzyl oxalate

Glpc analysis of the pyrolysate of di-α-methylbenzyl oxalate run at 570° showed the presence of at least eight

Table 22. Mass spectral data for bibenzyl from benzyl benzyl-α,α-$\underline{d}_2$ oxalate

	$\underline{m}/\underline{e}$	Intensity[a] of natural sample	Intensity[a] of deuterated sample	Calc'd peaks for $\underline{d}_0$	Calc'd peaks for $\underline{d}_1$	Calc'd peaks for $\underline{d}_2$	Calc'd peaks for $\underline{d}_3$	Calc'd peaks for $\underline{d}_4$
P	182	100	23.5	23.5	--	--	--	--
P+1	183	15.6	16.3	3.7	12.6	--	--	--
P+2	184	1.13	35.5	0.3	2.0	33.2	--	--
P+3	185		14.5	--	0.1	5.2	9.2	--
P+4	186		12.3	--	--	0.4	1.4	10.5

[a]Ionization voltage was 18 ev.

components. Nmr analysis showed that the components were styrene, benzaldehyde, dl and meso-2,3-diphenylbutanes, possibly formate of α-methylbenzyl alcohol and other unknowns. The identity of 2,3-diphenylbutanes was confirmed also by glpc peak enhancement (20% SE 30 column, 8' x 1/4", column temperature 135°). The ratio of styrene and 2,3-diphenylbutanes was based on nmr analysis. The relative ratio of the diastereomers was based on glpc peak areas, assuming their thermal conductivities are equal (60).

Pyrolysis of meso-2,3-diphenylbutane

A sample of meso-2,3-diphenylbutane was pyrolyzed at different temperatures using the usual method. The isomer ratio was obtained by nmr analysis (Table 5).

Pyrolysis of di-α-trifluoromethylbenzyl oxalate

Di-α-trifluoromethylbenzyl oxalate was pyrolyzed at 650° with a head temperature of 130-135°. Glpc analysis of the pyrolysate showed the presence of six components. The four components having the longer retention time were collected by glpc. Each component was then subjected to ir, nmr and mass spectral analyses. Both mass spectra of components A and B showed mass ion peak at m/e = 314 corresponded to the assigned structure, 2,3-diphenyl-1,1,1,4,4,4-hexafluorobutane. Glpc analysis was taken on a 20% SE 30 column (5' x 1/4", column temperature 190°) component

A (mp 73-75) and B (mp 156-158°) were assigned as dl and meso-2,3-diphenyl-1,1,1,4,4,4-hexafluorobutane respectively. The nmr and ir spectra of these two diastereomers are shown in Figures 4, 5, 6 and 7.

dl-2,3-diphenyl-1,1,1,4,4,4-hexafluorobutane

Anal. Calcd for $C_{16}H_{12}F_6$: C, 60.35; H, 3.82. Found: C, 60.49, H, 3.90.

meso-2,3-diphenyl-1,1,1,4,4,4-hexafluorobutane

Anal. Calcd for $C_{16}H_{12}F_6$: C, 60.35; H, 3.82. Found: C, 60.42; H, 3.84.

Component C was not identified, nmr spectrum showed peaks at δ, 7.43 (singlet) and 5.7-6.1 (multiplet). Ir spectrum showed C = 0 stretching frequency at 1770 cm^{-1}. The ratio of components A : B : C was 1 : 22 : 1.05 at 650° based on glpc analysis, assuming the thermal conductivity ratios are approximately the same. Approximately 40% of the 2,3-diphenyl-1,1,1,4,4,4-hexafluorobutane isomers were obtained from the pyrolysate based on nmr analysis using bibenzyl as an internal standard.

Pyrolysis of di-α-ethylbenzyl oxalate

Di-α-ethylbenzyl oxalate was pyrolyzed at 570° with a head temperature of 135-140°. Nmr analysis of the pyrolysate showed the presence of 0.76 mole of trans-methylstyrene, 0.026 mole of cis-methylstyrene, 0.31 mole

Figure 4. Nmr spectrum of dl-2,3-diphenyl-1,1,1,4,4,4-hexafluorobutane

Figure 5. Nmr spectrum of meso-2,3-diphenyl-1,1,1,4,4,4-hexafluorobutane

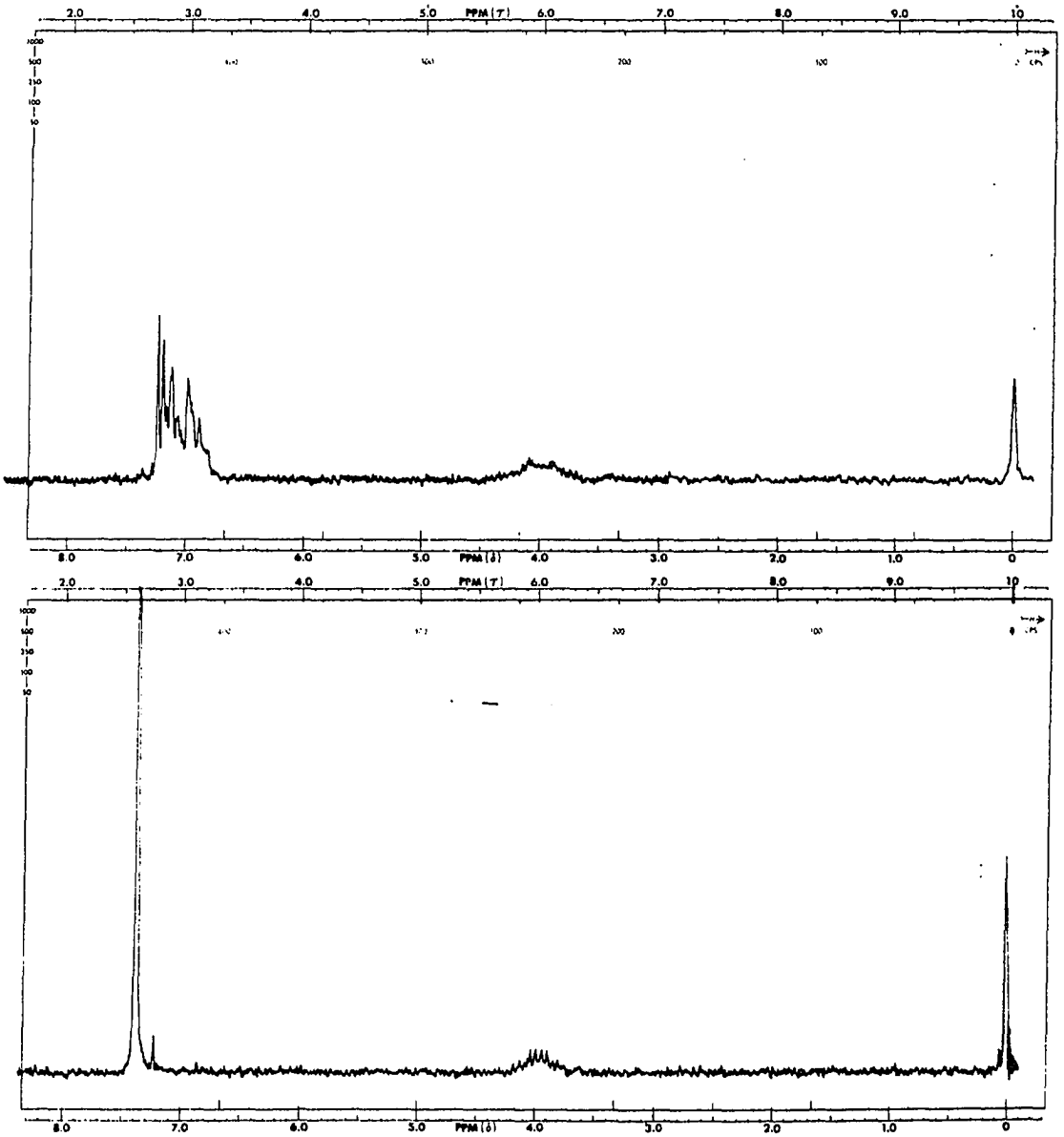
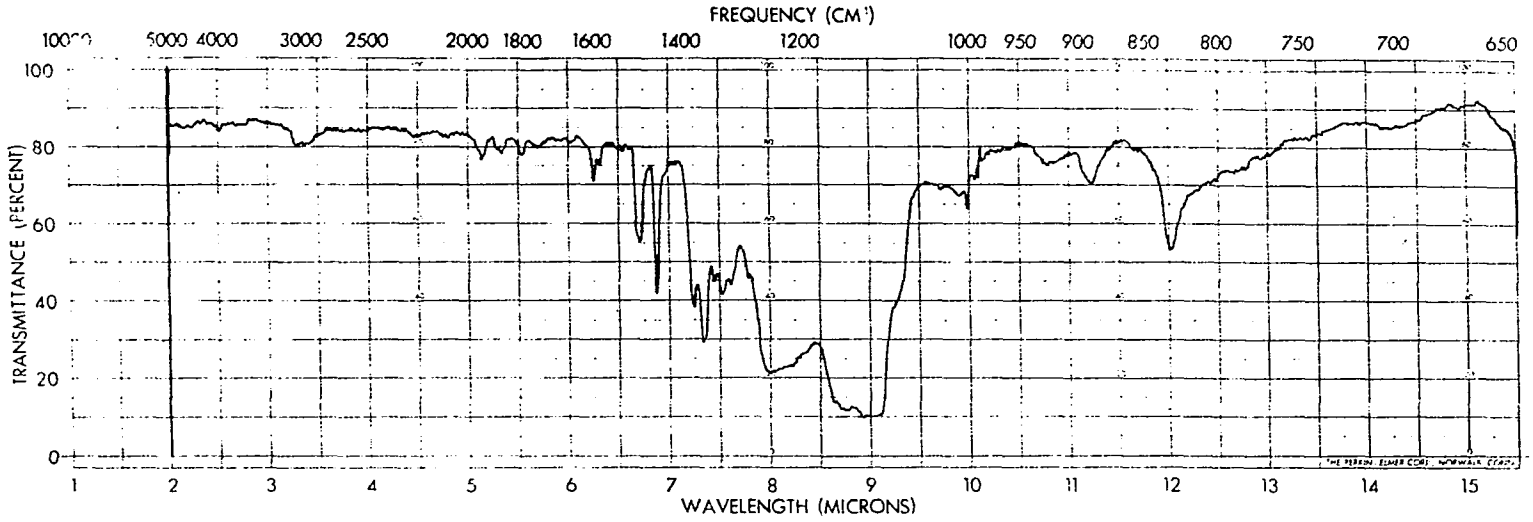
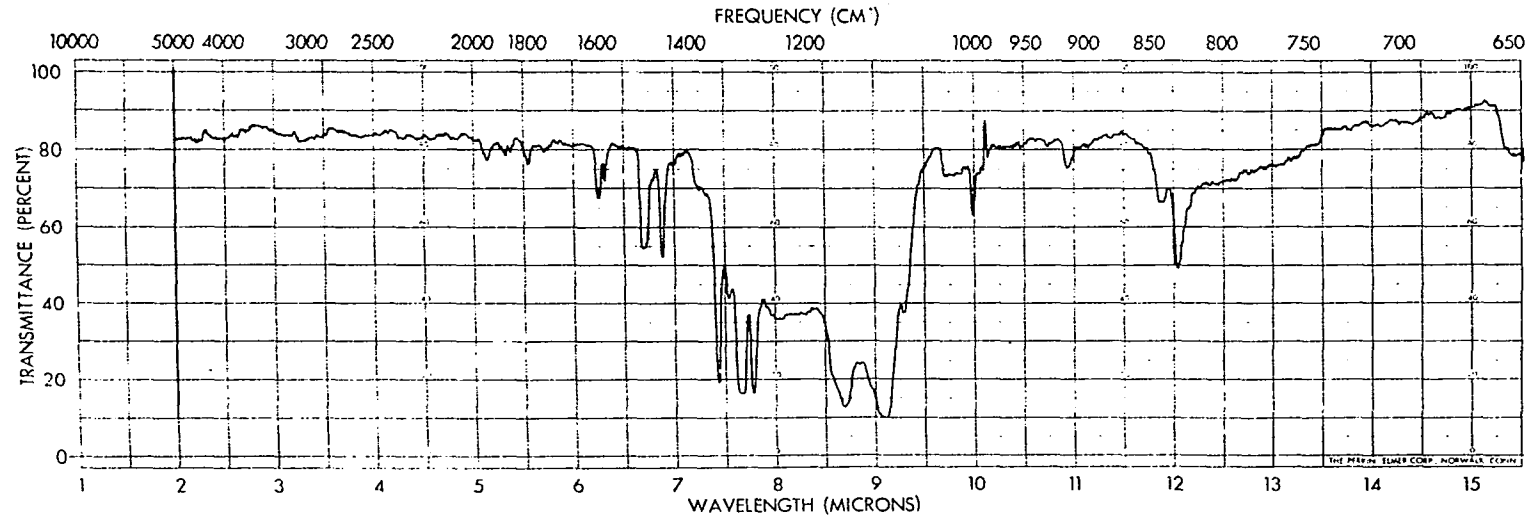

2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

Figure 6. Ir spectrum of dl-2,3-diphenyl-1,1,1,4,4,4-hexafluorobutane

Figure 7. Ir spectrum of meso-2,3-diphenyl-1,1,1,4,4,4-hexafluorobutane


FREQUENCY (CM⁻¹)
5000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)


FREQUENCY (CM⁻¹)
10000 5000 4000 3000 2500 2000 1800 1600 1400 1200 1000 950 900 850 800 750 700 650
TRANSMITTANCE (PERCENT)
100 80 60 40 20 0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
WAVELENGTH (MICRONS)

of styrene and other unknown components using dimethyl oxalate as an internal standard. The identity and ratio of the components were also confirmed by glpc analysis using a 20% SE 30 column (8' x 1/4", column temperature 90°).

Pyrolysis of di-α-isopropylbenzyl oxalate

Di-α-isopropylbenzyl oxalate was pyrolyzed at 570°. The glpc analysis of the pyrolysate indicated the presence of five components. They were identified by glpc peak enhancements. Nmr analysis of the pyrolysate using dimethyl oxalate as an internal standard showed that 0.36 mole of trans-β-methylstyrene and 0.905 mole of β-dimethylstyrene were formed per mole of oxalate pyrolyzed.

Pyrolysis of di-α-perfluoroethylbenzyl oxalate

Pyrolysis of di-α-perfluoroethylbenzyl oxalate took place at 650° with a head temperature of 135-140°. The characteristic nmr spectrum of the β,β-difluorostyrene was the main feature of the nmr spectrum of the pyrolysate (78). Nmr analysis showed that 1.5 moles of β,β-difluorostyrene was formed per mole of oxalate (based on bibenzyl as an internal standard). Glpc analysis of the pyrolysate showed the presence of at least three high boiling components in small amount (8' x 1/4" 20% SE 30 column).

Pyrolysis of di-α,α-dimethylbenzyl oxalate

The nmr spectrum of the pyrolysate run at 340° showed exclusively the characteristic spectrum of β,β-dimethylstyrene. Nmr analysis using bibenzyl as an internal standard showed that quantitative yield of the styrene was obtained. The identity of the product was further confirmed by glpc analysis (5' x 1/4" 20% SE 30).

Pyrolysis of α-t-butylbenzyl acetate

The nmr spectrum of the pyrolysate of α-t-butylbenzyl acetate run at 650° was quite complex. Glpc analysis of the pyrolysate on a 20% SE 30 (8' x 1/4" column temperature 125°) showed the presence of predominant amount of benzaldehyde and the starting material. Since the desired product was not present, no attempt was made to identify other unknowns.

Pyrolysis of diallyl oxalate

Small scale The pyrolysis of diallyl oxalate on a small scale is illustrated by the following run.

A sample of diallyl oxalate 0.89 gm (0.0052 mole) was placed in a glass boat in the closed end tube of the pyrolysis tube. This end was first cooled with dry ice. The system was then evacuated to 8 mm, with nitrogen bled through the system. The preheater was heated to 75°. Over a period

of 25 minutes, the oxalate was distilled through the hot tube heated to 635°. The vacuum was released and the pyrolysate was washed out of the trap by carbon tetrachloride into a 25 ml Erlenmeyer flask which contained 100.3 mg of naphthalene in 0.5 ml of carbon tetrachloride. Nmr spectrum of this solution showed peaks at δ. 7.1-7.9 (naphthalene) (multiplet), 6.3-5.23 (biallyl and biallyl oxalate) (multiplet) and 2.15 (biallyl)(triplet) in the ratio of 43 : 164 : 90. This gave a yield of 62.6% biallyl and a recovery of 8.08% biallyl oxalate. Biallyl from the pyrolysate was also confirmed by glpc peak enhancement using a Carbowax column (5' x 1/4").

Large scale Diallyl oxalate, 5.24 gm (.0308 mole) was placed in a specially designed 25 ml round bottom flask and attached to the pyrolysis tube by a standard taper ground joint. The other end of the pyrolysis tube was attached to a U-shaped trap made of 38 x 2.2 cm tubing with indentations which was connected to vacuum. The system was then evacuated to 3.0-3.5 mm with nitrogen bled through the system. The flask was heated to 60° by a zippered heating mantle. The pyrolysis took place for one hour at 660°. The pyrolysate was then transferred by a capilliary pipette directly into a 10 ml pear-shaped flask. Distillation by means of a short path distillation head gave 1.29 gm (.0157 mole) biallyl, 51.1% yield, bp 58-60° (lit.

(144) 59-60°).

Pyrolysis of di-trans-crotyl oxalate

Pyrolysis of di-trans-crotyl oxalate was carried out at 535°. Glpc analysis of the pyrolysate on a Silicon oil DC 550 column (6' x 1/4") at 60° showed the presence of two major products, a low boiling component, 3-methyl-1,5-heptadiene and 2,6-octadiene. The 2,6-octadiene and 3-methyl-1,5-heptadiene were confirmed by glpc peak enhancements and nmr spectrum. The ratio of these isomers was based on relative peak areas of the chromatogram.

Pyrolysis of di-trans-cinnamyl oxalate

A sample of di-trans-cinnamyl oxalate was pyrolyzed in the gas phase at 570° with a head temperature of 135-155°. The characteristic nmr spectrum of the indene was the main feature of the nmr spectrum of the pyrolysate. A known quantity of dimethyl oxalate was added to the pyrolysate as an internal standard. Integration of the methylene peak of indene and the methyl signal of the dimethyl oxalate showed that 0.82 mole of indene per mole of oxalate pyrolyzed was produced. Glpc analysis of the pyrolysate on a 20% SE 30 column (8' x 1/4", column temperature 90°) showed that per mole of oxalate pyrolyzed, 0.19 mole of styrene, 0.11 mole of trans-β-methylstyrene, 0.098 mole of allyl benzene, 0.014 mole of toluene and small amounts of two unknown

products were produced in addition to indene. It was also shown by glpc analysis that no indane was produced. It was assumed that the thermal conductivities of all the components are the same.

Pyrolysis of the oxalate at 650° gave very similar yields of the same products with the amount of indene being 0.86 mole per mole of oxalate.

Pyrolysis of trans-cinnamyl formate

Pyrolysis of trans-cinnamyl formate at 650° gave 0.82 mole of indene per mole of formate based on nmr analysis using bibenzyl as an internal standard. The glpc chromatogram of the pyrolysate was identical to that of the di-trans-cinnamyl oxalate pyrolysate. The relative ratio of the products was based on the peak areas of the components, assuming their thermal conductivities are the same.

Pyrolysis of trans-cinnamyl acetate

Pyrolysis of trans-cinnamyl formate at 650° gave 0.72 mole of indene per mole of acetate based on nmr analysis using bibenzyl as an internal standard. The glpc chromatogram of the pyrolysate was identical to that of the di-trans-cinnamyl oxalate pyrolysate. The relative ratio of the products was based on the peak areas of the components, assuming their thermal conductivities are the same.

Pyrolysis of di-trans-o-deuteriocinnamyl oxalate

Pyrolysis of di-trans-o-deuteriocinnamyl oxalate was carried out at 570° in the usual manner. Indene was isolated from the pyrolysate by glpc using 20% SE 30 column (8' x 1/4", column temperature = 78°). The indene was then submitted to mass spectral analysis for isotope purity. Pertinent mass spectral data are presented in Table 23. Mass spectral analysis showed that the indene contained 15.5 parts $\underline{d}_0$, 32.43 parts $\underline{d}_1$. After a correction of 8% of isotope impurity from the starting oxalate, an isotope effect of kH/kD = 2.94 was obtained.

Table 23. Mass spectral data for indene from pyrolysis of di-trans-o-deuteriocinnamyl oxalate

	m/e	Intensity of natural sample	Intensity of deuterated sample	Calc'd peak for $\underline{d}_0$	Calc'd peak for $\underline{d}_1$
P	116	100	15.5	15.5	
P+1	117	10.14	34.0	1.57	32.43
P+2	118	3.81	4.5	.59	3.29

Pyrolysis of di-trans-o-chlorocinnamyl oxalate

The pyrolysis of the oxalate was carried out in the usual manner with a head temperature of 160-165°, furnace temperature of 570°. Glpc analysis of the pyrolysate on a 20% Se 30 column (8' x 1/4", column temperature 80°) showed the presence of several components. Indene and 4-chloroindene were confirmed by their retention times. A ratio of 4-chloroindene/indene = 2.45 was obtained based on relative weights of the peak areas (assuming the thermal conductivity ratio is 1).

Pyrolysis of di-o-phenylbenzyl oxalate

Pyrolysis of di-o-phenylbenzyl oxalate at 640° with a head temperature of 160-165° gave 1.44 moles of fluorene and 0.025 mole of o-phenyltoluene per mole of oxalate based on glpc analysis on 20% SE 30 column (8' x 1/4", column temperature 175°) using bibenzyl as an internal standard. It was assumed that the thermal conductivities of bibenzyl and fluorene are equal. The yield of fluorene was also confirmed by nmr analysis using dibenzylsulfide as an internal standard.

Pyrolysis of methyl o-phenylbenzyl oxalate

Pyrolysis of this oxalate took place at 630° at 0.1 mm with a head temperature of 160-165°. The nmr spectrum of the pyrolysate showed the presence of fluorene as the major

product. Glpc analysis of the pyrolysate on a 20% SE 30 (8' x 1/4", column temperature = 180°) using bibenzyl as internal standard showed that 0.6 mole of fluorene was produced per mole of oxalate pyrolyzed. It was assumed that the thermal conductivities of fluorene and bibenzyl are equal.

Pyrolysis of di-o-phenoxylbenzyl oxalate

The di-o-phenoxylbenzyl oxalate was pyrolyzed at 650° with a head temperature of 165-170°. The nmr spectrum of the pyrolysate showed that 0.25 mole of xanthone, 0.05 mole of o-phenoxyltoluene and 0.05 mole of o-phenoxylbenzyl alcohol were formed per mole of oxalate using bibenzyl as an internal standard. The identity of xanthone was also confirmed by glpc analysis using 20% SE 30 (8' x 1/4", column temperature 195°).

Pyrolysis of di-o-benzylbenzyl oxalate

Di-o-benzylbenzyl oxalate was pyrolyzed at 570° with a head temperature of 175-180°. Glpc analysis of the pyrolysate on a 20% SE 30 column showed the presence of 9,10-dihydroanthracene and anthracene in the ratio of 1 : 1. Assuming both compounds have the same thermal conductivity. The nmr spectrum of the pyrolysate showed that 0.12 mole of 9,10-dihydroanthracene, 0.12 mole of anthracene and a trace of o-benzyltoluene were formed per mole of

oxalate pyrolyzed using bibenzyl as an internal standard.

Pyrolysis of dipropargyl oxalate

A sample of dipropargyl oxalate 150 mg (0.903 mmole) was placed in a glass container in the closed end tube. The system was evacuated to 0.5-0.7 mm and the furnace was heated to 660°. The preheater was heated to 70°. Approximately 20 minutes was required to sublime the oxalate over the pyrolysis tube. The pyrolysate in the trap was then washed out with carbon tetrachloride. Nmr spectrum of the pyrolysate (CCl_4) showed predominantly a sharp peak at δ, 7.25 corresponding to that of benzene's chemical shift and other minor peaks scattered through the region from 1.78 to 7.3δ. Since the desired product was not obtained, no attempt was made to identify the products.

Pyrolysis of catechol oxalate

Pyrolysis of catechol oxalate was carried out on the apparatus described below. The pyrolysis apparatus consisted of a Pyrex tube (18" x 3/4" O.D.) packed with 12" long of 3/32" (I.D.) glass helices. The tube was heated by Electric Apparatus Company's multiple unit electrical furnace (12" long). The furnace temperature was controlled by a Variac and was measured by an Iron-constantan thermocouple feeding into the Rubicon Company's recording potentiometer. One end of the thermocouple was encased in a

glass tube (1/8" x 4") and immersed in ice water. The pyrolysis was undertaken under an atmosphere of nitrogen. The nitrogen was passed through a column of molecular sieves before entering the pyrolysis tube and the flow rate was determined by means of a 5 ml hydrodermic syringe needle (2" long). The pyrolysis apparatus setup is shown in Figure 8. After each pyrolysis, air was passed through the hot tube (520-555^{o}) to remove any carbon deposits inside the tube.

Catechol oxalate-benzene solution was introduced through the septum cap fitted on top of the column by means of a syringe. The pyrolysate was collected in a trap and cooled by ice-water. Vapor phase chromatographic analysis of the pyrolysate on a 20% SF - 46 column (60/80 mesh, 5' x 1/4") indicated only one component, which was catechol carbonate.

The infrared spectrum of catechol carbonate ($CHCl_3$) showed C = O stretching at 1835 and 1845 cm^{-1} (s, doublet). The nmr spectrum (acetone) of catechol carbonate showed peak at δ 7.36 (s).

In a typical run, 57.3% of catechol carbonate was obtained from its oxalate, based on glpc anaysis using naphthalene as an internal standard. The thermal conductivity of naphthalene to that of catechol carbonate is 1.84

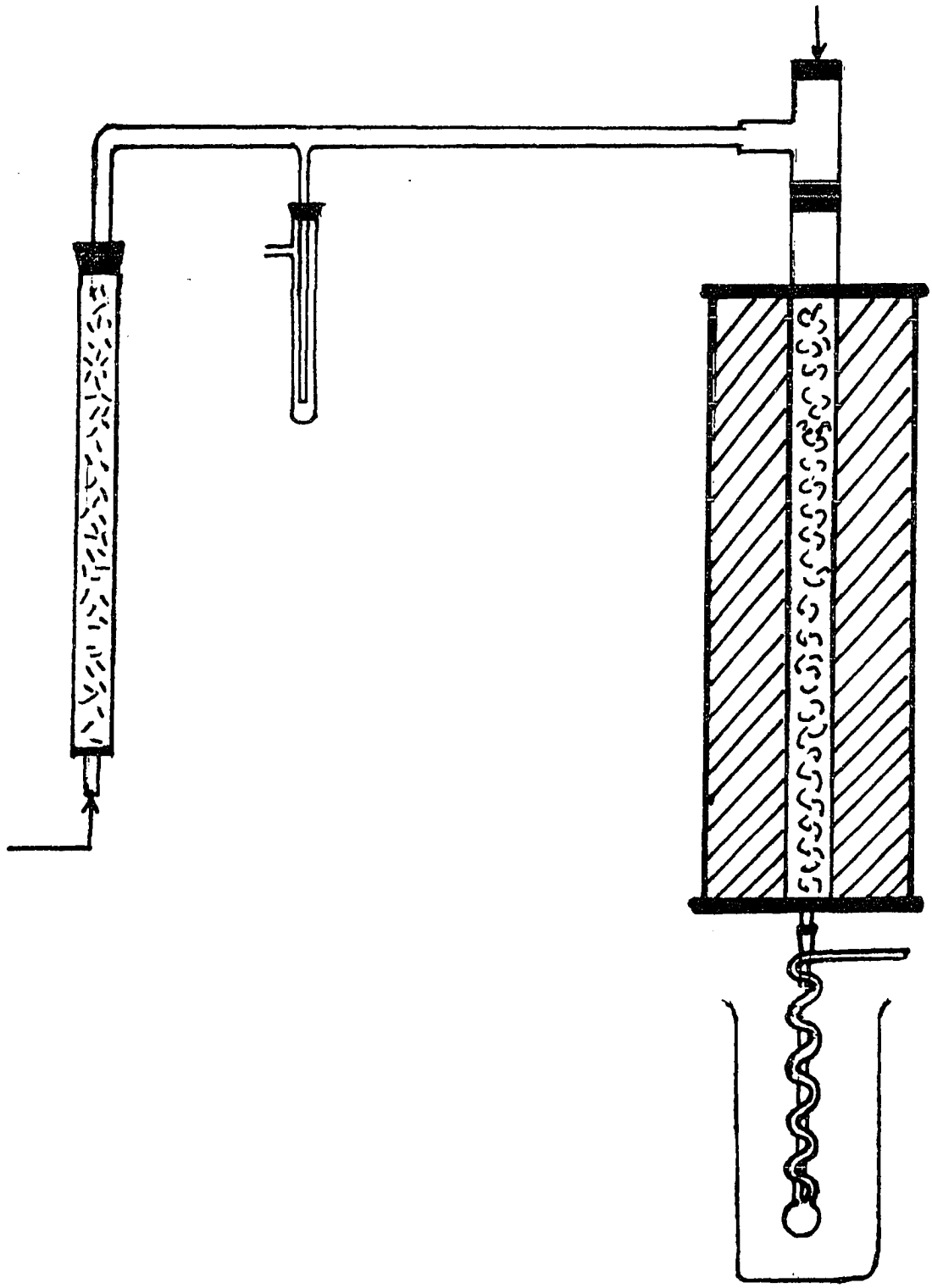


Figure 8. Pyrolysis apparatus for catechol oxalate

(weight basis). The glpc analysis was undertaken on a UCON column (HB 2000, 5' x 1/4", 60/80 mesh, column temperature 140^{o}).

SUMMARY

Good yields of bibenzyls were obtained by pyrolysis of dibenzyl oxalates under vacuum at 650°. Pyrolysis of unsymmetrical oxalates, benzyl p-chlorobenzyl oxalates and benzyl-benzyl-α,α-d_2 oxalate support an intermolecular mechanism involving coupling of benzyl radicals. The benzyl radicals may arise either from concerted three bond cleavage of the two alkyl carbon-oxygen bonds and the central carbon-carbon bond or from the two bond cleavage of the alkyl carbon-oxygen bond and the central carbon-carbon bond, followed by decarboxylation of the intermediate benzyloxycarbonyl radical.

Pyrolysis of organic oxalates in the gas phase offers a convenient way to generate stable radicals such as benzyl, allyl and cinnamyl radicals in the absence of reactive radicals or molecules.

Stereochemical aspects of radical coupling were studied. A (meso/dl) ratio of 2,3-diphenylbutanes equal to (52/48) was obtained from the coupling of α-methylbenzyl radicals. This indicates that α-methylbenzyl radicals undergo coupling without stereochemical preference. A (meso/dl) ratio of 2,3-diphenyl-1,1,1,4,4,4-hexafluorobutane equal to (29/71) was obtained from the coupling of α-trifluoromethylbenzyl radicals. The stereospecificity observed in the coupling of these fluorinated radicals may be accounted for on the basis of the

polar nature of the trifluoromethyl groups.

Radicals generated from α-alkylbenzyl oxalates undergo β scission exclusively to give olefins if there is a β-alkyl group present. Considerable amounts of olefins are also formed from the pyrolysis of this type of oxalates presumably arising from a concerted cyclic elimination pathway.

Intramolecular cyclization of cinnamyl radical forms predominantly indene. Pyrolysis of other appropriate oxalates gave respectively products of cyclization like fluorene, xanthene and 9,10-dihydroanthracene. This shows another synthetic utility of oxalate pyrolysis. A deuterium isotope effect of k_H/k_D of 2.94 was obtained from the cyclization of o-deuteriocinnamyl radical. It is concluded that substantial carbon-hydrogen bond cleavage occurs at the transition state. Probably, a fast equilibrium between the cinnamyl radical and the intermediate cyclic radical is followed by the slow hydrogen atom abstraction step.

A ratio of 2,6-octadiene/3-methyl-1,5-heptadiene equal to 52.4/47.6 was obtained from the pyrolysis of di-trans-crotyl oxalate. Benzene was the predominant product obtained from the pyrolysis of dipropargyl oxalate.

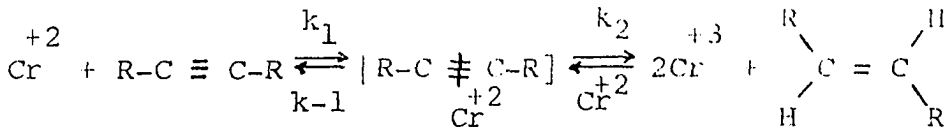
Catechol oxalate gave catechol carbonate upon pyrolysis. In this oxalate, oxygen-carbonyl carbon bond cleavage occurs rather than the alkyl carbon-oxygen bond cleavage in dibenzyl oxalates.

PART II. REACTIONS OF CHROMIUM(II) WITH ORGANIC OXALATES

INTRODUCTION

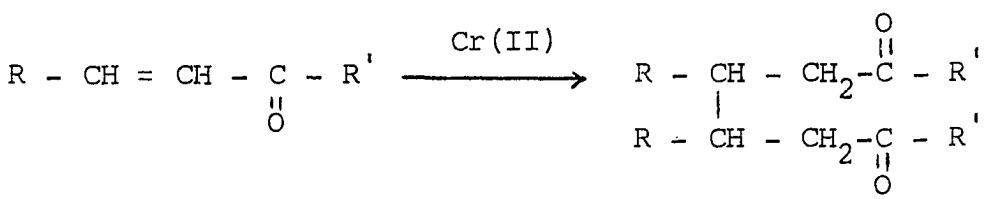
Chromium(II) salts are the most powerful reducing agents used as standard solutions in quantitative analysis. The standard potential of the couple, Cr(III) + e ⇄ CR(II) is -0.41 volts (146). Chromium(II) is easily oxidized, so the reaction solution should always be excluded from the air. Since chromium(II) ion in aqueous solution has a sky-blue color, while chromium(III) solution is greenish color (or other colors depending on the ligand), it is quite convenient to follow the reaction of chromium(II).

The first use of chromium(II) as a reducing reagent for organic compounds was reported by Berthelot a century ago (147). Traube and Passarge (148) have also shown that ammoniacal as well as acidic chromium(II) chloride reacted with acetylene to give olefin. Recently, it was reported that homogeneous reduction of acetylene by chromium(II) sulfate in water or aqueous dimethylformamide gave trans olefins in high yield. The stoichiometry, stereospecificity, kinetics and reactivities of the acetylenes toward chromium(II) are in accord with a mechanism which involves a rate determining attack of chromium(II) upon a 1 : 1 acetylene-chromium(II) complex (149, 150).



Aqueous solution of acidic chromium chloride were reported to reduce maleic or fumaric acid to succinic acid and cinnamic acid to hydrocinnamic acid (148). These conversions were also effected with chromium(II) hydroxide (151, 152). A mechanism analogous to that advocated for the reduction of acetylenes was proposed by Castro et al. (153) for the reduction of olefins.

Typical aromatic aldehydes, α,β-unsaturated aldehydes, benzalacetophenones and certain other α,β-unsaturated ketones are reduced by chromium(II) with the formation of bimolecular product resulting from reductive coupling (154, 155, 156).



Unusual reactivity has been shown by chromium(II) in concentrated aqueous ammoniacal solution. Benzaldehyde and acetophenone are converted to their corresponding alcohols (157). Other compounds like acrylonitrile, acrylic acid and acrylamide which are not affected by acidic chromium(II) solution are rapidly reduced by ammoniacal

chromium(II). Neither the acidic nor ammoniacal chromium(II) reagent affects the aliphatic ketones or cinnamyl alcohol (156). It has been noted that oxalic acid was reduced to glycolic acid by chromium(II) perchlorate instantaneously (158).

The σ-bond organochromium compounds have been studied actively during recent years (159, 160). Reaction of chromium(II) halide on ethyl ether gives compounds of the structure $CrX_2OC_2H_5$. Similar compounds are formed

X = Cl, Br, I

$$2CrX_2 + 2C_2H_5OC_2H_5 \longrightarrow 2CrX_2OC_2H_5 + C_4H_{10}$$

with dioxane and benzyl ethyl ether, except aromatic ethers. Aniline, pyridine and piperidine produce diamino complexes of the type $CrX_2OC_2H_5$ $(Amine)_2$.

Several chemists (161, 162, 163) have shown the existence of benzylchromium complex by spectroscopic means and investigated the kinetics of its formation. Benzylchromium complex is formed by the reaction of benzyl halides with aqueous chromium(II) perchlorate in perchloric acid. Bibenzyl was formed from the benzylchromium complex through

$$ArCH_2Cl + Cr(II) \xrightarrow{slow} ArCH_2\cdot + Cr(III)Cl^{+2}$$

$$ArCH_2\cdot + Cr(II) \xrightarrow{fast} ArCH_2Cr^{+2}$$

coupling, while the toluene from protonolysis in acidic solution (164).

$$ArCH_2Cr^{+2} + X^- \longrightarrow ArCH_2CrX^+$$

$$ArCH_2CrX^+ + H^+ \longrightarrow ArCH_3 + CrX^{+2}$$

Anet (165) has also reported the formation of chloropentaaquochromium(III) perchlorate and $[Cr(H_2O)_5^{+2}CHCl_2]$ from reactions of chloroform and chromium(II). Homogeneous reduction of organic halides such as α-substituted benzyl,

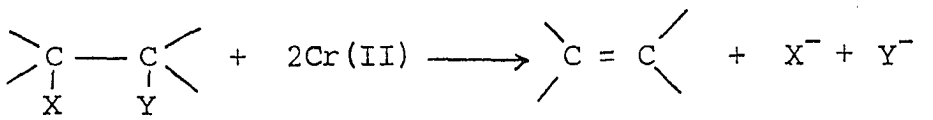
$$CHCl_3 + 2Cr^{+2} + 10H_2O \longrightarrow Cr(H_2O)_5Cl^{+2} + Cr(H_2O)_5CHCl_2^{+2}$$

benzhydryl and allyl have shown to give high yields of dimeric products upon reaction with acidic chromium(II) (166, 167, 168).

The reaction of alkyl halides is considered one of the practical use of chromium(II) reduction on organic compounds (169, 170). Elimination or protonolysis products could be obtained depending upon the structure and reactivity of the halides. On the other hand, halides with an adjacent halogen, hydroxyl or other anionic substituents give rise to olefins.

Recently, Kochi et al. have shown that ethylenediamine chromium(II) is an effective reagent for reductive elimina-

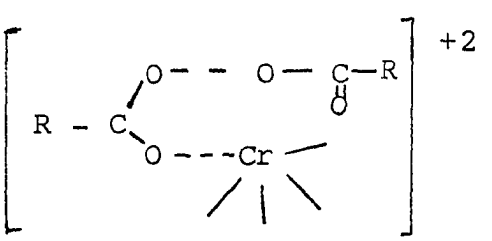
tion of vicinal dihalides or other β-substituted halides to the alkenes in high yield. Epoxides as well as episulfides were also reduced to alkenes effectively (171).



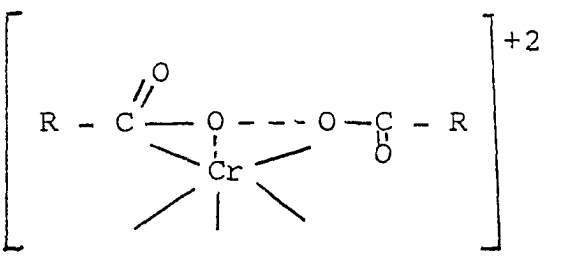
X = halogen, Y = HO, AcO, NH_2

A subtle application of reduction of organic halides by chromium(II) was the dehalogenation of steroids reported by Julian and Barton (172, 173). Reductive cyclization of α,ω-dihaloalkanes by chromium(II) to cyclopropane is another synthetic application of chromium(II) (174).

It has been reported (175) that alphatic diacyl peroxides are readily reduced by two equivalents of chromium (II) to alkane, carbon dioxide and carboxylato chromium(III) salts. The mechanism of this reduction is described in terms of a transition state involving ligand transfer of XXIII or XXIV.



XXIII

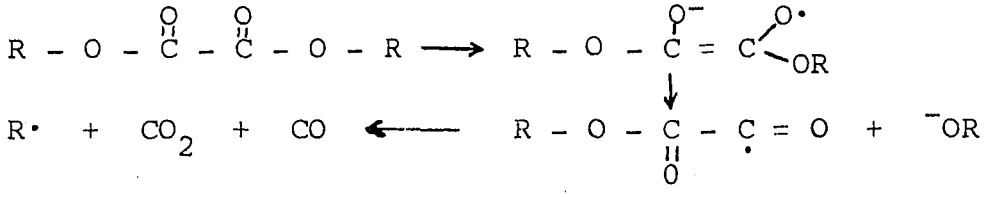


XXIV

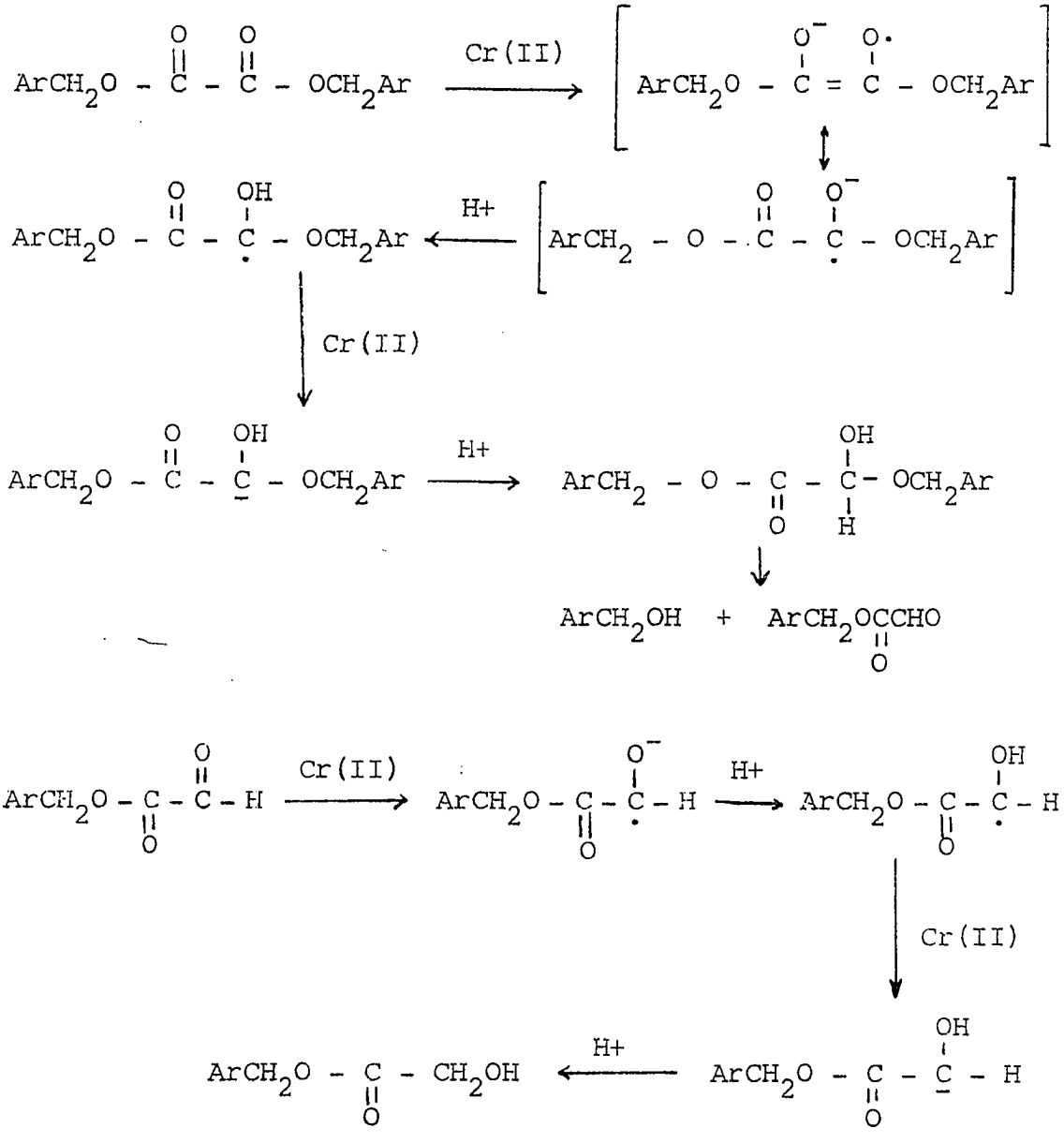
It is of considerable interest to investigate the reactivity of chromium(II) toward organic oxalates so as to compare to other carbonyl compounds.

RESULTS AND DISCUSSION

In continuation of our work with organic oxalates, the reaction of chromium(II) with benzyl oxalate was undertaken. It was reported that oxalic acid reacts instantaneously with chromium(II) to give exclusively glycolate (158). Since the reactivity of the chromium(II) depends greatly on the pH of the solution, the enhanced rate of this reaction compared to other α,β-dicarbonyl compounds might be due to the acidity of the oxalic acid. It is interesting to investigate the reactivity as well as products obtained from reaction of chromium(II) with organic oxalate. The reaction of dibenzyl oxalate with chromium(II) might go through a radical anion intermediate (III) and could generate benzyl radical.



Reaction of dibenzyl oxalate with chromium(II) sulfate in aqueous dimethylformamide solution gave a mixture of benzyl alcohol and benzylglycolate in the ratio of 3 : 2. A reasonable mechanistic scheme for the product formation is as follows:



By this reaction scheme, equal amounts of benzyl alcohol and benzyl glycolate should be formed. The fact that more benzyl alcohol was obtained may be attributed to some other side reactions, possibly hydrolysis of benzyl glycolate under

the reaction conditions or simultaneous reduction of the two carbonyl groups of the intermediate benzyl glyoxalate. When benzyl glycolate and benzyl alcohol was stirred with chromium(III) dimethylformamide solution, the relative ratio of ester and alcohol remained the same. However when benzyl glyoxalate was reacted with chromium(II), benzyl alcohol and benzyl glycolate were formed in the ratio of 1 : 2. This showed that during the course of reaction, approximately 50% of the intermediate glyoxalate also underwent reduction in the ester carbonyl group leading to ethylene glycol and benzyl alcohol. It was also found that the same ratio of ester and benzyl alcohol was obtained from the reduction of methyl benzyl oxalate. Thus the products obtained from the oxalate reduction are analogous to that obtained from oxalic acid with enhanced reaction rate also. It is interesting to note that oxalate gave the reduction compound, but an α-keto acid like pyruvic acid gave bimolecular product (154).

EXPERIMENTAL

Chemicals and Sources

Tartaric acid (Matheson Coleman), chromium(III) sulfate XH_2O (Matheson Coleman), zinc dust (Baker), lead tetraacetate (Matheson Coleman).

Preparations and Reactions

Preparation of chromium(II) sulfate reagent

Chromium(II) sulfate was prepared according to the method of Castro (166) and standardized as described.

Reaction of dibenzyl oxalate with chromium(II)

Benzyl oxalate (139) 0.68 gm (.0025 mole) was dissolved in 35 ml of dimethylformamide in a 250 ml round bottom flask fitted with septum. The solution was then degassed for one hour. Chromium(II) solution (20 ml) was then introduced with a syringe needle. A greenish coloration appeared in the reaction mixture immediately. The reaction mixture was kept under nitrogen atmosphere for 2 1/2 hours. Water (60 ml) was added to the mixture and was extracted with ether (3 x 100 ml). The ethereal solution was further extracted with water (80 ml, 100 ml), dried over magnesium sulfate, and concentrated to give a liquid residue. Thin layer chromatography of this residue on a 8" x 8" plate coated

with silica gel ($PF_{254+366}$) using a mixture of Skelly B and ether (75 : 85) showed three bands by UV lamp detection. The silica gel bands were then scraped off and stirred in ether separately in a round bottom flask. The ether was then filtered and evaporated. The first band from the bottom was identified as benzyl glycolate. The nmr spectrum ($CDCl_3$) showed peaks at δ, 7.35 (s, 5H), 5.28 (s, 2H), 4.18 (d, 2H), 2.45 (broad singlet, 1H). The ir spectrum showed strong OH absorption at 3510 cm^{-1} and C = O absorption at 1740 cm^{-1}. The other components were identified as benzyl alcohol and benzyl oxalate by nmr analysis also.

In another run, when the reaction mixture was allowed to stand for 26 hours, nmr analysis of the reaction mixture (using bibenzyl as internal standard) showed 0.51 mole of benzyl glycolate and 0.73 mole of benzyl alcohol per mole of oxalate.

Preparation of dibenzyl ester of tartaric acid

The ester was prepared according to the method of Patterson (176).

Preparation of benzyl glyoxalate

Benzyl glyoxalate was prepared by a lead tetra-acetate method (177) except the product was not isolated in its pure form.

Reaction of benzyl glyoxalate with chromium(II) solution

Approximately 6.84 gm of crude benzyl glyoxalate was dissolved in 35 ml of dimethylformamide in a 250 ml round bottom flask. The reaction mixture was then stoppered with septum and degassed for an hour. Chromium(II) (30 ml) solution was then introduced into one flask with a hyperdermic syringe. The reaction mixture was then stirred for four more hours. Water (100 ml) was then added and extracted with ethyl ether (3 x 80 ml). The ethereal solution was dried over magnesium sulfate and concentrated to give a liquid residue. Nmr analysis of this residue showed that ca. a ratio of 23 : 11 of benzyl glycolate and benzyl alcohol was obtained.

Reaction of methyl benzyl oxalate (25) with chromium(II)

The reaction procedure was similar to that of the reaction of dibenzyl oxalate. Nmr analysis of the residue showed a ratio of 2 : 3 of benzyl alcohol and benzyl glycolate.

SUMMARY

Dibenzyl oxalate was reduced by chromium(II) sulfate in aqueous dimethylformamide solution to give benzyl glycolate and benzyl alcohol in the ratio of 2 : 3. It was also found that the benzyl glyoxalate undergoes reduction to give benzyl alcohol and benzyl glycolate (1:2). Presumably, dibenzyl oxalate undergoes reduction by chromium(II) through a benzyl glyoxalate intermediate which is then reduced further either to the glycolate or undergoes simultaneous reduction of the two carbonyl groups to give benzyl alcohol and ethylene glycol.

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ACKNOWLEDGMENTS

The author wishes to express her profound appreciation to Dr. W. S. Trahanovsky for his advice, guidance and encouragement throughout the period of her graduate study.

Thanks are due to the members of the Trahanovsky group, who have provided an entertaining atmosphere in the laboratory and supplied moral support.

To Mr. D. K. Wells, a special thank you is due for his helpful discussions and proof reading of this manuscript.