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Thermal decomposition of organic oxalates, tritylazocarboxylates, and triphenylacetates

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THERMAL DECOMPOSITION OF ORGANIC OXALATES, TRITYLAZOCARBOXYLATES, AND TRIPHENYLACETATES

by

Douglas Edward Zabel

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

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Iowa State University
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INTRODUCTION

After preparing a new compound one of its first reactions a chemist might investigate because of the simplicity of the technique is the fate of the compound when it is heated in an inert atmosphere to the point of decomposition. Virtually every type of organic compound from saturated hydrocarbons to polyfunctional molecules has been studied under pyrolytic conditions. Esters of monocarboxylic acids have been very actively investigated, and much is known about the nature of the pyrolytic decomposition of these esters.

Quite surprisingly, very little effort has been expended upon determining the products and nature of the pyrolytic decomposition of esters of dicarboxylic acids, in particular, oxalate esters, even though probably thousands of such esters have been synthesized; furthermore, most of the work which has been done in this area antedates 1927, long before the advent of modern separation and identification methods.

In the past very little mention of a class of free radicals which we prefer to name alkoxycarbonyl or aryloxycarbonyl radicals $(R\text{-}O\overset{O}{\overset{\|}{C}}\cdot)$ has been made or implied in the chemical literature. Occasionally the alkoxycarbonyl or aryloxycarbonyl radical is postulated as a possible intermediate in a decomposition mechanism, but not much can be found concerning a convenient method for generating this radical, and not much is known about its properties.

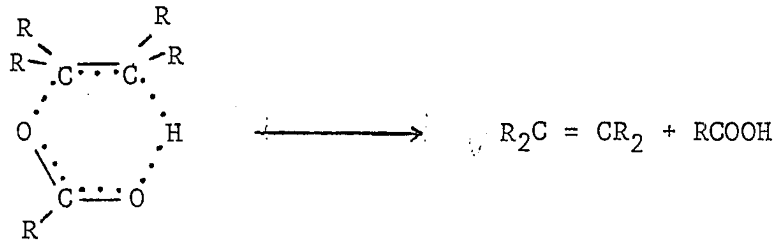
Another species rarely encountered in the literature is the α-lactone intermediate; to my knowledge, in only one instance has the α-lactone intermediate been fairly well documented.

In this thesis will be presented evidence that alkoxycarbonyl and aryloxycarbonyl radicals are intermediates in the thermal decomposition (200 - 560°) of benzhydryl oxalates and can be readily generated from the thermal decomposition (60 - 75°) of tritylazocarboxylates. It will also be argued that the transient α-lactone species is an intermediate in the thermal decomposition (350°) of benzyl and methyl triphenylacetates.

HISTORICAL

For well over a century esters have been known to decompose when heated at 300 - 550° into olefins and carboxylic acids (48). In 1960 the accumulated data on these pyrolytic eliminations were sorted and evaluated for the first time in a review by DePuy and King (32). The results of many experiments (1, 3, 5, 6, 14) have established the β-*cis* nature of this pyrolytic elimination, the work of Curtin and Kellom (27) being the most elegant demonstration of this point. The direction of elimination and the relative amounts of products formed on pyrolyses of esters which lead to two or more possible olefins are dependent in ofttimes subtle ways on the interplay of several factors (32): statistical effects, depending upon the number of possible conformations with a β-*cis* hydrogen which will give rise to a particular olefin upon pyrolysis; steric effects, favoring formation of terminal and *trans* olefins and hindering formation of internal and *cis* olefins; thermodynamic effects, favoring production of the more stable isomeric olefin provided statistical and steric effects are equal; and substituent effects, being small to modest in extent, the interpretation of which being as yet open to debate.

If one envisions a cyclic, concerted mechanism for pyrolysis of esters, first proposed by Hurd and Blunck (50), one can readily account for the unimolecular, *cis* character of the reaction and for its negative entropy of activation (Scheme 1). This mechanism seems to be generally accepted as the major path for decomposition, but there are many questions about the detailed nature of the transition state left unanswered.

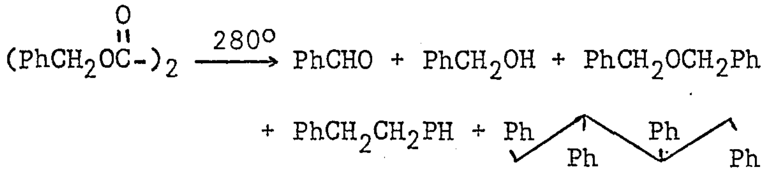


Scheme 1. Mechanism of ester pyrolysis

From the data on hand concerning the details of the process (32, 91), the best picture that can be drawn of the transition state for the pyrolysis of esters is that of a highly concerted elimination in which only a small role can be assigned to charge separation, in which some double bond character has developed between the carbon atoms, and which is relatively insensitive to resonance or inductive effects.

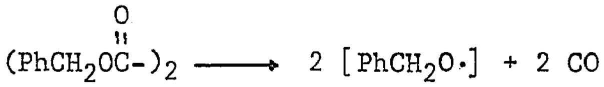
About 1850, Malaguti (66) and Cahours (23) reported that pentachloroethyl oxalate and trichloromethyl oxalate decompose at 250 - 400° to give carbon monoxide and phosgene plus other products. Around 1900, several workers (37, 82) found that ethyl oxalate decomposed thermally to give mainly carbon dioxide, carbon monoxide, and olefins. Ethylene oxalate was pyrolyzed (87) at 240° to yield 40% of ethylene and carbon dioxide, 28% of ethylene carbonate and carbon monoxide, and 24% of ethylene glycol acetal of acetaldehyde. Other cyclic oxalates which have been pyrolyzed are glyceryl oxalate and trimethylene oxalate (87, 88).

In a more recent study on the mechanism of the Bacon reaction 20 gm of benzyl oxalate (71) was kept at 280° for 6 hr under reflux. Upon distillation of the pyrolysate under reduced pressure 2.0 gm of benzaldehyde, 2.0 gm of benzyl alcohol, and 2.2 gm of benzyl ether were isolated (equation 1). Bibenzyl and polybenzyl were also found.

(1) 

$$(PhCH_2O\overset{O}{\overset{\|}{C}}-)_2 \xrightarrow{280^o} PhCHO + PhCH_2OH + PhCH_2OCH_2Ph + PhCH_2CH_2PH + \ldots$$

To account for the equimolar amounts of benzaldehyde and benzyl alcohol formed, a benzoxy radical was proposed as an intermediate which then disproportionated to give benzaldehyde and benzyl alcohol; benzyl alcohol then underwent dehydration to form benzyl ether (equations 2-4).

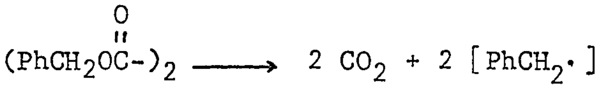
(2) 

$$(PhCH_2O\overset{O}{\overset{\|}{C}}-)_2 \longrightarrow 2\ [PhCH_2O\cdot] + 2\ CO$$

(3) $$2\ [PhCH_2O\cdot] \longrightarrow PhCHO + PhCH_2OH$$

(4) $$2\ PhCH_2OH \longrightarrow PhCH_2OCH_2Ph + H_2O$$

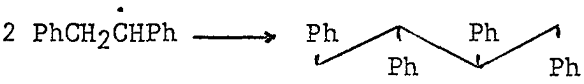
Benzyl radicals are also postulated as intermediates in this pyrolysis and can couple to form bibenzyl and polybenzyl (equations 5-8).

(5) 

$$(PhCH_2O\overset{O}{\overset{\|}{C}}-)_2 \longrightarrow 2\ CO_2 + 2\ [PhCH_2\cdot]$$

(6) $$2[PhCH_2\cdot] \longrightarrow PhCH_2CH_2Ph$$

(7) $$2\ PhCH_2CH_2Ph \longrightarrow 2\ PhCH_2\overset{\bullet}{C}HPh + 2\ H\cdot$$

(8) 

$$2\ PhCH_2\overset{\bullet}{C}HPh \longrightarrow$$

Conversion of benzyl oxalates to the corresponding bibenzyls in high yield has been reported[1] using pyrolysis in the gas phase. Pyrolyses of the unsymmetrical oxalates, benzyl 4-chlorobenzyl oxalate and benzyl benzyl-$\underline{\alpha,\alpha\text{-}d_2}$ oxalate, indicate that the mechanism of the reaction requires statistical scrambling of the benzyl groups, an observation consistent with the formation of benzyl radicals.

In a series of aliphatic and alicyclic oxalates (53) tertiary oxalates both neat and in quinoline solution decomposed readily at 140 - 160° to yield 80 - 100% of the corresponding olefins, whereas primary and secondary oxalates resisted decomposition at least up to 325°. At temperatures above 210° formate esters were observed to accompany olefin formation. No skeletal rearrangements except in bornyl cases were noticed. The composition of the olefin products resembles the mixture of isomers obtained upon acid catalyzed and dimethyl sulfoxide dehydrations of alcohols (Saytzeff-like eliminations) rather than the mixture of isomers obtained by ester and xanthate pyrolyses (Hofmann-like eliminations). These results seem to indicate the operation of an ion pair mechanism.

Among the types of compounds which might give rise to alkoxycarbonyl radicals are the esters of azoformic acid. When dimethyl azodiformate was heated in boiling naphthalene for a long period of time (84), 65 - 70% of the theoretical amount of nitrogen was evolved; the major decomposition products were carbon monoxide and dimethyl carbonate as well

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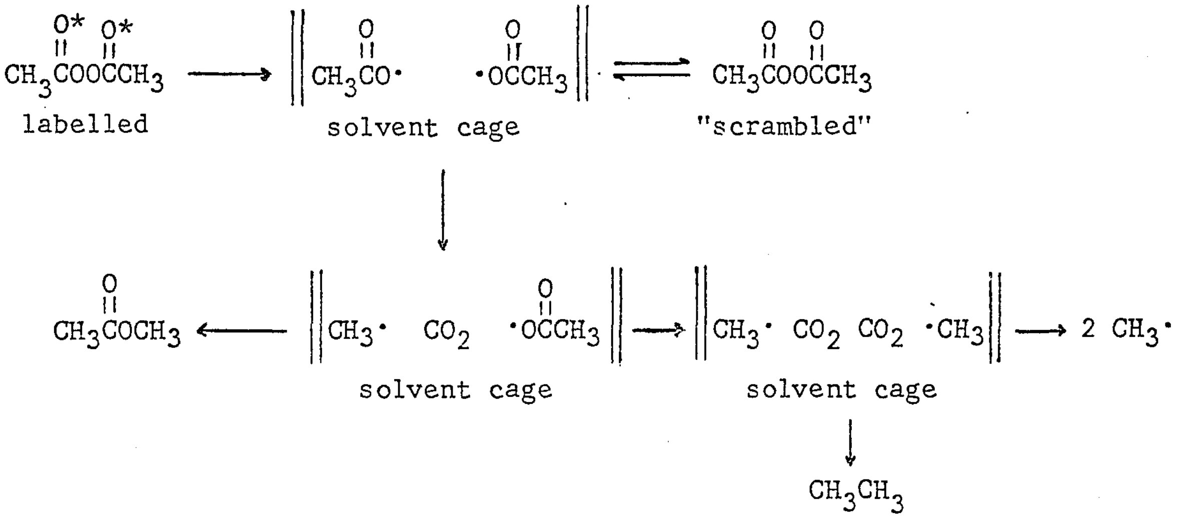
[1] W. S. Trahanovsky, C. C. Ong, and J. A. Lawson, Ames, Iowa. Private communication (1968).

as a small amount of dimethyl oxalate. No other experimental details were given. It seems reasonable to suppose that the methoxycarbonyl radical could be an intermediate in this decomposition.

Dimethyl azodiformate was also irradiated at -196° and examined by electron spin resonance techniques (4). In the esr spectrum evidence for methyl radicals could be seen; also observed was a narrow asymmetrical singlet peak possibly due to the presence of methoxy radicals or methoxycarbonyl radicals. Ethyl azodiformate has been found (44) to be fairly stable to ultraviolet radiation but does slowly decompose into ethylene and carbon dioxide.

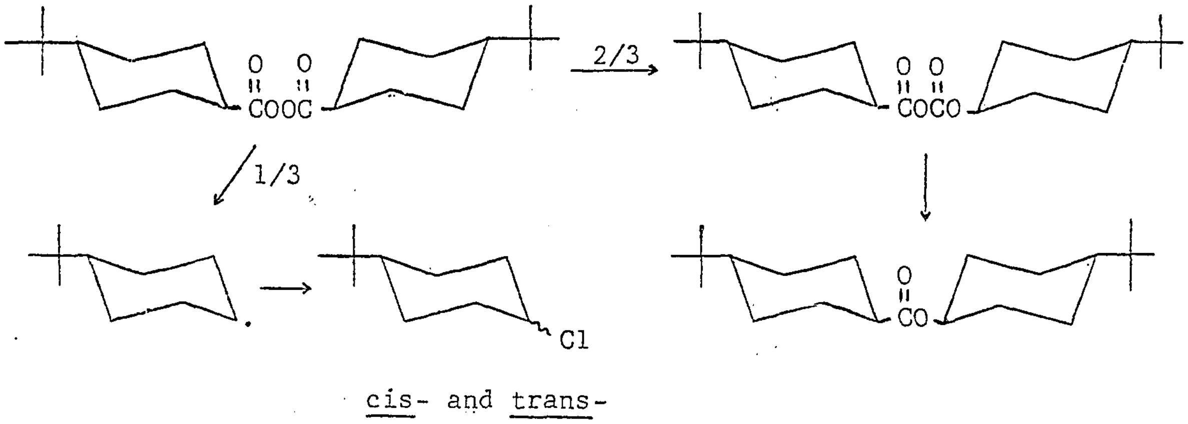
Decomposition studies of ethyl and benzyl t-butylperoxyoxalates as well as di-t-butyl monoperoxyoxalate (11, 8) demonstrated that alkoxycarbonyl radicals are stable enough to escape from the solvent cage, to be trapped by molecules of solvents such as benzene or cumene or by molecules of a scavenger such as galvinoxyl, and to abstract a hydrogen atom from some active hydrogen-donating species such as cumene. It was also noted that only 17% of the ethoxycarbonyl radicals escaping the solvent cage decarboxylated before being trapped, while 87-98% of the t-butoxycarbonyl radicals escaping the solvent cage decarboxylated; therefore, the greater the stability of the alkyl radical R· formed, the greater will be the rate of decarboxylation of the alkoxycarbonyl radical ($\mathrm{RO\overset{O}{\overset{\|}{C}}\cdot}$).

The alkylcarboxy radical ($\mathrm{R\overset{O}{\overset{\|}{C}}O\cdot}$), a close relative of the alkoxycarbonyl radical, is thought to be generated by the thermal decomposition of diacyl peroxides. Thermal decomposition had usually been considered to proceed by initial homolytic cleavage (28, 29, 33, 39, 45, 47, 54, 57, 58, 89) of the O-O bond and/or direct conversion of peroxide to ester which is frequently a major product by trapping the carboxy radical. Recent publications by Taylor and Martin (85, 86) on the thermal decomposition of acetyl peroxide support this mechanism for this peroxide. Their isotopic tracer methods involving use of acetyl-carbonyl-^{18}O peroxide and deuterium-labelled acetyl peroxide provide evidence for a large amount (~38%) of cage recombination of acetoxy radicals forming acetyl peroxide and for a clean (> 99%) intramolecular recombination of decarboxylated radicals leading to ethane and methyl acetate (Scheme 2).



Scheme 2. Decomposition of acetyl peroxide

Another mode of ester formation has recently been demonstrated (40); in some aliphatic diacyl peroxide systems the major decomposition pathway in nonpolar media is via rearrangement to alkyl alkanecarbonyl carbonates which upon further heating are converted in high yield to esters. Thus, about two-thirds of the diacyl peroxide, trans-4-t-butylcyclohexanecarbonyl peroxide (Scheme 3), rearranges to trans-4-t-butylcyclohexyl trans-4-t-butylcyclohexanecarbonyl carbonate before decomposing to carbon dioxide and ester, while the remaining one-third cleaves homolytically to yield alkyl radicals trapped as cis- and trans-4-t-butylcyclohexyl chloride. Acetyl peroxide does not follow this carboxy-inversion process on the route to methyl acetate (86).



Scheme 3. Major decomposition pathway for some aliphatic diacyl peroxides

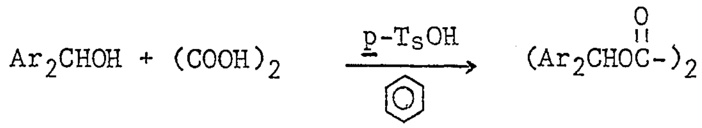
Another approach to the generation of the carboxy radical is through the thermal decomposition of t-butylperoxy esters. Using iodine as a radical trap homolytic decomposition of t-butylperoxy phenylacetate has been shown to be entirely concerted (13); essentially no carboxy radical could be trapped. Phenyl-substituted t-butylperoxy phenylacetates (12) follow σ^+, which can only mean that the fragment being stabilized is the benzyl free radical and not the more distant phenylacetoxy free radical. Another series of t-butyl peresters (10) undergo thermal decomposition at rates which parallel the stability of the free radical R· in the formula RCOOO-t-Bu. Evidently thermal decomposition of these esters involves simultaneous rupture of the O-O and C-C bonds, carbon dioxide being formed in the primary step. Again there was no evidence of carboxy radicals being trapped.

RESULTS AND DISCUSSION

Pyrolysis of Benzhydryl Oxalates

Whereas the pyrolyses of monocarboxylic acid esters have been actively and extensively investigated for a long time (32), and a great many intimate details are known about the mechanism of this process, next to nothing has been reported[1] concerning the nature of the products or the process involved in the pyrolyses of dicarboxylic acid esters, in particular, oxalate esters.

For our studies systems containing no β hydrogens that could lead to elimination were chosen. A simple, general synthetic procedure patterned after that of Lespagnol (59) was used for preparing symmetrical benzhydryl oxalates in 70-80% yield; these oxalates can be prepared in the presence of p-toluenesulfonic acid as catalyst by refluxing for a minimum of 6 hr the corresponding benzhydrol and oxalic acid in benzene, azeotroping the water formed during the esterification away from the reaction site with the benzene (equation 9). Concentrated sulfuric acid was found to be an unsatisfactory catalyst in the preparation of 4,4'-dichlorobenzhydryl oxalate; only a viscous liquid was produced, and none of the desired oxalate could be found.

(9) 

$$\mathrm{Ar_2CHOH + (COOH)_2 \xrightarrow{\underline{p}\text{-TsOH}} (Ar_2CHO\overset{O}{\overset{\|}{C}}-)_2}$$

Hexane proved to be a better choice for recrystallization of

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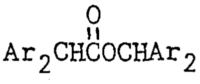
[1] See Historical section.

4,4'-dichlorobenzhydryl oxalate than carbon tetrachloride, for the oxalate incorporates two molecules of carbon tetrachloride per molecule of oxalate in the crystal structure, producing puzzling analyses as well as a broad mp range.

Thermal decomposition (as evidenced by evolution of gas) of benzhydryl and 4,4'-dichlorobenzhydryl oxalates required a minimum temperature of 200 - 210°. Decomposition of benzhydryl oxalate in phenyl ether proceeded at a convenient rate at 225°; the half life was <2 hr. At temperatures $>300°$ the neat oxalates decomposed almost explosively.

The two major nonvolatile products from the neat decomposition of these oxalates at 275° were isolated by column chromatography and were proved to be the corresponding tetraarylethane and benzhydryl diarylacetate; their yields are presented in Table 1. Also isolated from the

Table 1. Products isolated by column chromatography from the pyrolysis of neat benzhydryl and 4,4'-dichlorobenzhydryl oxalates at 275°

Product	From benzhydryl oxalate, %	From 4,4'-dichlorobenzhydryl oxalate, %
$Ar_2CHCHAr_2$	57	55
 $Ar_2CH\overset{O}{\overset{\|}{C}}OCHAr_2$	21	27
Ar_2CHOH[a]	7	9

[a] Yield based on 2 moles of benzhydrol from each mole of oxalate.

pyrolysates were small amounts of the corresponding benzhydrols. Close scrutiny by nmr of the pyrolysate before column chromatography showed that benzhydrol was not a product of the pyrolysis. Upon passing through a chromatography column the oxalate did produce benzhydrol, but the diphenylacetate did not; therefore, the benzhydrol obtained from the pyrolysate must come from hydrolysis of undecomposed oxalate on the chromatography column.

The yields of products obtained from other decomposition studies of benzhydryl oxalate neat and in phenyl ether solution were calculated from the data in Tables 18 and 19 and are presented in Table 2.

The presence of benzhydryl radicals is strongly indicated from the following results. When oxygen, a well-known interceptor of alkyl radicals (78), was bubbled through benzhydryl oxalate, either neat or in phenyl ether solution, heated at 225°, the yields of tetraphenylethane and benzhydryl diphenylacetate were drastically reduced; benzophenone and benzhydryl ether, reasonable products of radical trapping by oxygen, were found instead. The possibility that oxygen was destroying the tetraphenylethane and benzhydryl diphenylacetate after they were formed can be dismissed in the light of the observation that at least 90% of a mixture of tetraphenylethane and benzhydryl diphenylacetate was recovered unchanged when subjected to pyrolysis conditions (225° for 1 hr) in the presence of oxygen. The intermediacy of benzhydryl radicals is also supported by the observation in deuterium-labelling experiments (*vide infra*) that tetraphenylethane is produced by an intermolecular

Table 2. Yields of decomposition products from benzhydryl oxalate

Run	Temp, °C	Period of heating, hr	Yields,[a] % TPE[b]	BHDPA[c]
1	225	2	43	10
2	225	2	41	10
3	225	10	62	16
4[d]	200	2	17	16
5[d]	200	2.25	20	16
6[d,e,f]	225	1	5.3	6.3
7[e,g]	225	1	0	0

[a] Products were analyzed by nmr using diphenylmethane as an internal standard.

[b] TPE--1,1,2,2-tetraphenylethane.

[c] BHDPA--benzhydryl diphenylacetate.

[d] Pyrolysis of neat benzhydryl oxalate; others pyrolyzed in phenyl ether solution.

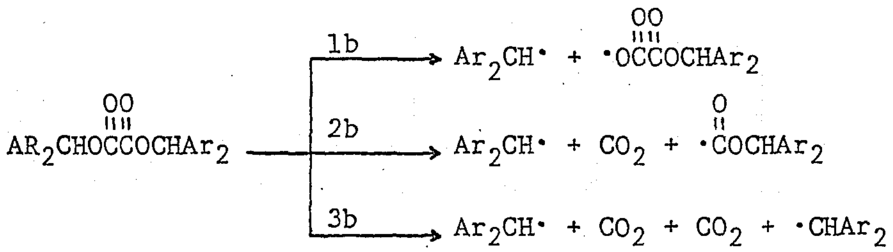
[e] Pyrolysis was carried out in the presence of oxygen.

[f] The major product (~ 45%) was benzophenone; 5% benzhydryl ether was obtained.

[g] Presumably benzophenone is the major product, but it could not be quantitatively determined by nmr because of the solvent, phenyl ether.

process. Coupling of two free benzhydryl radicals most reasonably accounts for this result. These two facts would seem to eliminate from consideration any heterolytic bond-cleavage pathways to products and to favor free radical pathways to products.

There are then three reasonable mechanisms involving homolytic cleavage of bonds and leading to benzhydryl radicals which can be written for the thermal decomposition of benzhydryl oxalate (Scheme 4). Follow-



$$\mathrm{AR_2CHO\overset{O}{C}\overset{O}{C}OCHAr_2} \xrightarrow{1b} \mathrm{Ar_2CH\cdot + \cdot O\overset{O}{C}\overset{O}{C}OCHAr_2}$$

$$\xrightarrow{2b} \mathrm{Ar_2CH\cdot + CO_2 + \cdot\overset{O}{C}OCHAr_2}$$

$$\xrightarrow{3b} \mathrm{Ar_2CH\cdot + CO_2 + CO_2 + \cdot CHAr_2}$$

Scheme 4. Possible mechanisms for the thermal decomposition of benzhydryl oxalate

ing path 1b, a one-bond cleavage produces a benzhydryl radical and an acyloxy radical. Path 2b, involving two-bond cleavage, leads to a benzhydryl radical, one molecule of carbon dioxide, and an alkoxycarbonyl radical. Simultaneous cleavage of three bonds gives two benzhydryl radicals and two molecules of carbon dioxide.

Phenyl oxalate experienced only negligible decomposition when heated at 350° for 0.5 hr; it can be concluded, therefore, that thermolysis of benzhydryl oxalate must initially involve cleavage of the benzhydryl--oxygen bond. The thermal instability of the benzhydryl oxalate is due to the formation of the stable benzhydryl radical, but the formation of the unstable phenyl radical from phenyl oxalate would not be favored, and this oxalate is more stable thermally. Greater steric repulsion between the benzhydryl groups could not account for the large stability difference observed.

Simultaneously the central carbon--carbon bond in benzhydryl oxalate must cleave since benzhydryl diphenylacetate can be heated at 225° for 1.25 hr with essentially no decomposition. One-bond cleavage (path 1b) would predict that benzhydryl oxalate and benzhydryl diphenylacetate should cleave at approximately the same rate because the stability of the two acyloxy radicals and relief of steric repulsions should be about the same. It might also be pointed out that the central oxalate bond is probably weak since it joins two positively polarized atoms (8).

The high yield of benzhydryl diphenylacetate obtained from decomposition of benzhydryl oxalate negates the possibility of concerted cleavage of three bonds (path 3b).

Attempts to induce decomposition of benzhydryl oxalate either neat or in benzene solution by supplying a good source of benzhydryl radicals did not produce any benzhydryl diphenylacetate. The source of the benzhydryl radicals, t-butylperoxy diphenylacetate, gave only the products expected from decomposition of the peroxy ester (9); no significant loss of oxalate was observed.

The presence of benzhydryl diphenylacetate suggests that the unusual radical, benzhydroxycarbonyl ($Ph_2CHO\overset{O}{\overset{\|}{C}}\cdot$), has sufficient stability to be successfully trapped. Very little is known about the nature and properties of alkoxycarbonyl radicals, but Bartlett[1] (11, 8) has shown them to exist as "stable" entities. The related acyloxy radical, $\mathrm{R}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{O}\cdot$, appears to be a much more transient species.[2,3]

In the absence of any induced decomposition by benzhydryl radicals, the initial step in the decomposition of benzhydryl oxalates must be a thermally induced, concerted, homolytic cleavage of two bonds (path 2b).[4]

In order to ascertain whether the formation of the two main products was inter- or intramolecular, a 50:50 mixture of benzhydryl and benzhydryl-$\underline{\alpha\text{-}d_1}$ oxalates in phenyl ether was decomposed.

If either product were formed via a concerted, cyclic, and hence intramolecular mechanism, or if either were formed in some necessarily intramolecular process within the solvent cage, no d_1-isotope product can be formed, or in other words, the ratio of the corrected peak heights for d_0, d_1, and d_2 should be 1:0:1. If either product were formed randomly from radicals which are essentially "free" in solution, one-half of the product will contain one deuterium, one-quarter will contain no deuterium, and one-quarter will contain two deuteriums. The ratio of corrected peak heights for d_0, d_1, and d_2 should then be 1:2:1.

The isotope distributions of the two products were determined by

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[1] P. D. Bartlett, Boston, Mass. Private communication. 1967.

[2] See Historical section.

[3] J. C. Martin has recently reported (85, 86) that acetoxy radicals do exist in a "solvent cage".

[4] During our investigation, we became aware of a related study on oxalates by Professor J. Warkentin and D. M. Singleton. These workers reached the same conclusion from kinetic measurements on the thermolysis of substituted benzhydryl oxalates.

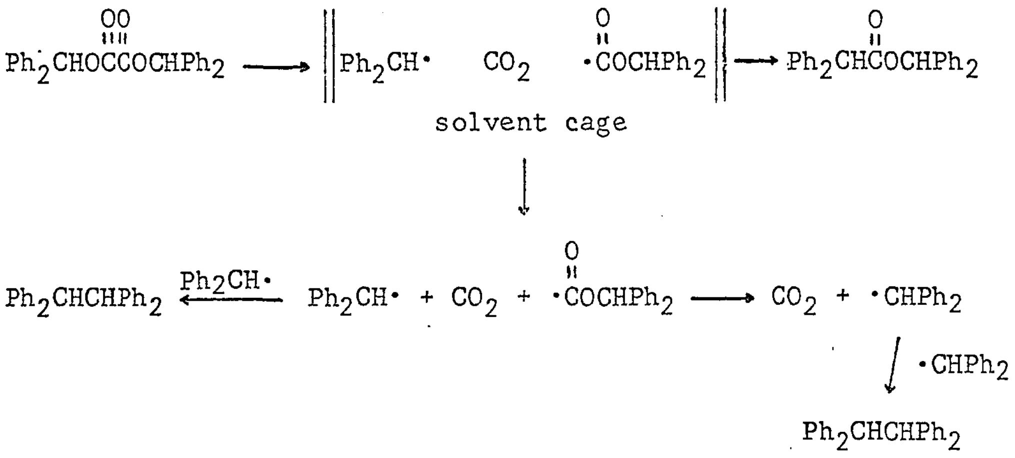
mass spectral analysis, and in Table 3 the isotope distributions calculated from the data in Tables 20 and 21 are presented.

Table 3. Isotope distribution in products from pyrolysis of an equimolar mixture of benzhydryl and benzhydryl-α-d_1 oxalates in phenyl ether at 225°

Product	d_0, %	d_1, %	d_2, %
1,1,2,2-Tetraphenylethane	24	45	31
Benzhydryl diphenylacetate	54	14	32

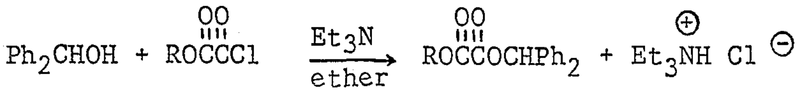
The inequality of the d_0 and d_2 values is somewhat of a mystery, since care was taken to start out with exactly a 50:50 mixture of the d_0 and d_2 oxalates. Experimental error in measuring the weak molecular ion peaks of benzhydryl diphenylacetate may be a cause of the inequality of these d_0 and d_2 values. Although mass spectral analyses were run at as low an ionization voltage as possible (17 eV), fragmentations occurred even then. Since the d_0 and d_2 peaks were approximately equal, no large isotope effect during fragmentation could have existed. Moreover, the relative ratios of the d_0, d_1, and d_2 peaks did not change appreciably from low to high ionization voltages.

The major pathway to tetraphenylethane must involve an intermolecular reaction, whereas the major pathway to benzhydryl diphenylacetate must involve an intramolecular process. These pathways cannot be the sole modes of formation of these products, for the isotope distributions observed are not exactly those calculated for inter- and intramolecular reactions. The major pathway to tetraphenylethane and benzhydryl diphenylacetate is readily accommodated by path 2b which leads to the initial formation of a benzhydryl radical, one molecule of carbon dioxide, and a benzhydroxycarbonyl radical. Coupling of the two radicals in a cage reaction leads to the intramolecular formation of the ester. The stability of the benzhydroxycarbonyl radical must be great enough to permit its capture in the solvent cage, and it must be stable enough to diffuse out of the cage, since a small amount of the ester is formed intermolecularly. However, only a little ester is formed intermolecularly; this must mean that the radical rather quickly decomposes to a benzhydryl radical and a molecule of carbon dioxide. Scheme 5 seems to be the best representation of the fate of benzhydryl oxalate molecules when heated in phenyl ether solution.



Scheme 5. Mechanism of thermolysis of benzhydryl oxalate in phenyl ether

Unsymmetrical oxalates were readily prepared from benzhydrol and half esters of oxalyl chloride in the presence of triethylamine (equation 10). Benzyl oxalyl chloride reacted with benzhydrol to yield 84%

(10) 

$$Ph_2CHOH + RO\overset{O}{\overset{\Vert}{C}}\overset{O}{\overset{\Vert}{C}}Cl \xrightarrow[ether]{Et_3N} RO\overset{O}{\overset{\Vert}{C}}\overset{O}{\overset{\Vert}{C}}OCHPh_2 + Et_3\overset{\oplus}{N}H\ Cl^{\ominus}$$

$R = PhCH_2-$ or CH_3-

of benzyl benzhydryl oxalate, and reaction of methyl oxalyl chloride with benzhydrol produced an 84% yield of methyl benzhydryl oxalate.

The decomposition products and yields from samples of benzyl benzhydryl oxalate in phenyl ether which were degassed and sealed under vacuum are given in Table 4, using the data in Table 22.

Since oxalates are decomposed during column chromatography and are either decomposed on or will not pass through an SE-30 glpc column (used for high boiling compounds), the amount of undecomposed oxalate could not be directly measured and must be estimated from a combination of nmr and glpc data.

The benzhydryl methinyl absorption in the nmr is totally obscured by the intense phenyl ether signal; therefore, the benzylic proton absorption must be corrected for the absorption due to the methinyl (1 H) and benzylic protons (2 H) of benzyl diphenylacetate, since all of these signals in phenyl ether appear at $\sim 5.0\,\delta$. The yield of benzyl diphenylacetate was obtained by glpc analysis and was converted into a correction factor for the benzylic proton absorption in the nmr.

Although large numbers of free benzyl and benzhydryl radicals appear to be present during the pyrolysis, as evidenced by the coupling products, 1,1,2,2-tetraphenylethane and 1,1,2-triphenylethane and the hydrogen-abstraction product, toluene, detection of benzyl diphenylacetate

Table 4. Major decomposition products[a] of benzyl benzhydryl oxalate in phenyl ether

Compound	Moles/mole oxalate Run 1[b]	Run 2[c]
Original oxalate	1.00	1.00
Toluene[d]	0.045	0.085
1,1,2-Triphenylethane[d]	0.104	0.146
Benzyl diphenylacetate[d]	0.181	0.286
1,1,2,2-Tetraphenylethane[d]	0.154	0.154
Remaining oxalate[e]	0.36	0.051

[a] Products were identified by peak enhancement (nmr and glpc).

[b] Heated at 245° for 11.5 hr; amount of oxalate pyrolyzed--0.196 mmole.

[c] Heated at 235° for 89 hr; amount of oxalate pyrolyzed--0.209 mmole.

[d] Values were determined by glpc analysis using benzil as an internal standard.

[e] Values were determined by nmr analysis using diphenylmethane as an internal standard.

as the major product argues strongly for the existence of benzoxycarbonyl radicals during pyrolysis.

Having established that the major decomposition pathway for symmetrical benzhydryl oxalates (Scheme 2) involves simultaneous cleavage of two of the three possible bonds in the oxalate moiety, two different alkoxycarbonyl radicals, the benzoxycarbonyl radical and the benzhydroxycarbonyl radical, are possible from the decomposition of benzyl benzhydryl oxalate.

Since no benzhydryl phenylacetate was detected and since the benzhydryl radical is considerably more stable than the benzyl radical. and should form in preference to the benzyl radical, two-bond cleavage giving a benzoxycarbonyl radical and a benzhydryl radical should be the favored process. Indeed, because of this stability difference two-bond cleavage to yield a benzhydroxycarbonyl radical and a benzyl radical may never occur.[1]

If some of the alkoxycarbonyl radicals from the benzyl benzhydryl oxalate decomposition escape from the solvent cage as some of them must certainly have done during the pyrolysis of benzhydryl oxalate (Scheme 2), there exists the possibility that two such radicals could couple, producing benzhydryl oxalate and/or benzyl oxalate. Benzhydryl oxalate, if formed, would not be expected to survive under these pyrolysis conditions (235° for 89 hr). When degassed, vacuum-sealed samples of benzyl oxalate were heated under these conditions, 82% of the original benzyl oxalate was recovered, along with a small amount of crystalline material insoluble in phenyl ether even at high temperatures (presumably polybenzyl (71)).

Although benzyl oxalate could survive under these pyrolysis conditions, its formation does not seem likely; alkoxycarbonyl radicals have not exhibited any ability to couple with one another (p. 34).

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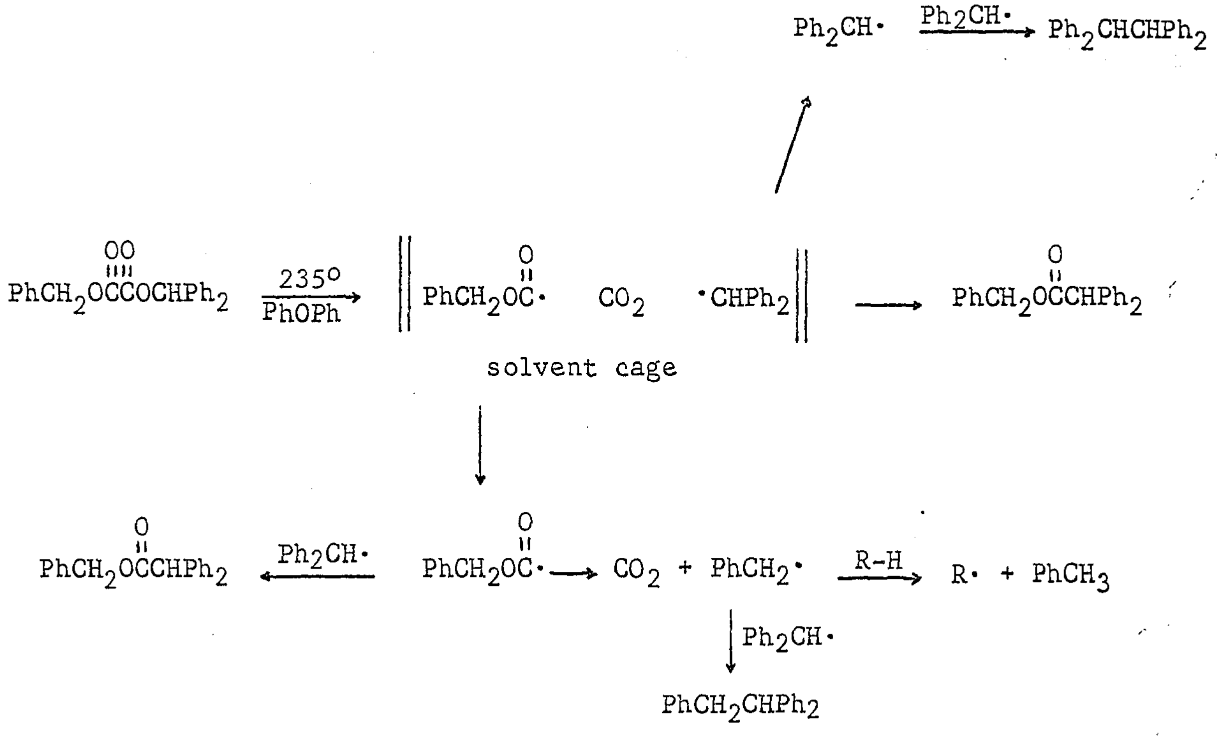
[1] An alternative to this mechanism which has not been eliminated from consideration and which would lead to the same observed results is as follows. The conclusion that the greater the stability of the radical R· produced, the greater will be the rate of decarboxylation of ROOC· (8) would predict that the benzhydroxycarbonyl radical leading to the more stable benzhydryl radical would be less stable toward decarboxylation than the benzoxycarbonyl radical leading to the benzyl radical.

From the run for 89 hr (Table 4) one can determine the fate of 0.119 mmole (57%) of the benzyl half of the molecule and of 0.154 mmole (74%) of the benzhydryl half of the molecule. The exact fate of the missing material is unknown, but presumably radical addition into the solvent (76) could occur and would account for the missing benzyls and benzhydryls, for these adducts would probably have very high boiling points and would not pass through an SE-30 glpc column. Some of the unidentified products present in small amount would account for a portion of this material.

In the following Scheme 6 a partial explanation of the observations made is presented.



Scheme 6. Partial mechanism for the decomposition of benzyl benzhydryl oxalate in phenyl ether

Pyrolysis of methyl benzhydryl oxalate in the gas phase led to the products listed in Table 5. The yields were calculated from the nmr data in Table 24; the assumption was made that the number of moles of benzhydryl groups in the original oxalate equaled the number of moles of benzhydryl groups recovered as nonvolatile pyrolysis products. A typical nmr spectrum used for analysis is shown in Figure 2 (p. 93).

Table 5. Products from the gas phase pyrolysis of methyl benzhydryl oxalate

Compound	Run 1[a]	Run 2[b]	Run 3[c]	Run 4[d]	Run 5[e]	Run 6[f]
Original oxalate	1.00	1.00	1.00	1.00	1.00	1.00
1,1,2,2-Tetraphenylethane	--	--	0.06	0.12	0.15	0.04
Diphenylmethane	--	--	--	0.06	0.17	0.06
Recovered oxalate	0.86	0.94	0.78	0.54	0.04	0.24
Methyl diphenylacetate	--	--	--	--	0.01	--
Methyl benzhydryl ether	0.14	0.06	0.13	0.19	0.06	0.03
1,1-Diphenylethane	--	--	0.03	0.10	0.57	0.63

[a] Pyrolyzed at 400° and 0.07 mm; 0.394 mmole of oxalate used.

[b] Pyrolyzed at 400° and 3.1 mm; 0.370 mmole of oxalate used.

[c] Pyrolyzed at 400° and 2.4 mm; 0.378 mmole of oxalate used.

[d] Pyrolyzed at 450° and 2.2 mm; 0.285 mmole of oxalate used.

[e] Pyrolyzed at 500° and 2.2 mm; 0.277 mmole of oxalate used.

[f] Pyrolyzed at 560° and 0.08 mm; 0.378 mmole of oxalate used.

Pyrolysis in the gas phase[1] offers the distinct advantage of studying thermal decompositions without any appreciable solvent cage effect and was chosen for the study of methyl benzhydryl oxalate decomposition.

The physics of the vacuum pyrolysis apparatus are very complicated and also unknown; therefore, two important and related variables, the average length of time each molecule spendsin the pyrolysis tube and the pressure inside the pyrolysis tube, were not known and could not be precisely controlled in order to optimize yields.

Thus, at 400° and pressures ranging from 0.07 to 3.1 mm methyl benzhydryl ether was the major, if not only, decomposition product, but large amounts of methyl benzhydryl oxalate were recovered unchanged.

As the temperature was raised, more oxalate was destroyed, but a new major product, 1,1-diphenylethane, appeared, less methyl benzhydryl ether was formed, and other products complicated the pyrolysate.

1,1-Diphenylethane obviously must come about from the coupling of a methyl radical and a benzhydryl radical, while 1,1,2,2-tetraphenylethane must come from two benzhydryl radicals. The coupling product of two methyl radicals, ethane, would be too volatile to be detected. Diphenylmethane must arise as a result of a hydrogen abstraction by a benzhydryl radical from some unknown precursor.

By analogy with the finding that the ethoxycarbonyl radical is more stable toward decomposition than the t-butoxycarbonyl radical (8), the methoxycarbonyl radical would be expected to survive much longer than the benzhydroxycarbonyl radical. At 400° the methoxycarbonyl radical de-

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[1] W. S. Trahanovsky, C. C. Ong, and J. A. Lawson, Ames, Iowa. Private communication. 1968.

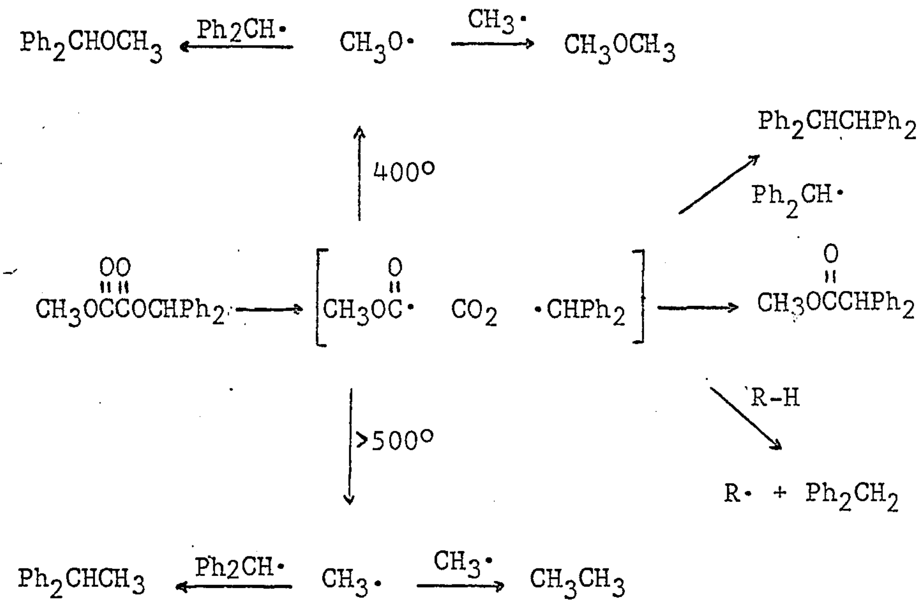
composes primarily by decarbonylation to the methoxy radical, and this radical then couples with an available benzhydryl radical to form the relatively nonvolatile substance, methyl benzhydryl ether. At 500° or more the predominant mode of decomposition of the methoxycarbonyl radical involves decarboxylation to give the methyl radical followed by reaction with other radical species.

The formation of methoxycarbonyl radicals is further supported by the observation that methyl diphenylacetate, the product of the coupling of a methoxycarbonyl radical and a benzhydryl radical, was found in small yield, but no benzhydryl acetate from the coupling of a benzhydroxycarbonyl radical and a methyl radical was noted.

Scheme 7 depicts a reasonable mechanism for the decomposition of methyl benzhydryl oxalate. The fragments of the oxalate enclosed in brackets are shown before they have moved very far from one another, for it is possible that methyl diphenylacetate arises from a gas phase cage effect. The efficiency of the cage effect in this case is now known, but an appreciable gas phase cage effect has been observed in the decomposition of azomethane (64).

In view of the simplicity of this procedure, pyrolysis of substituted benzhydryl methyl oxalates may provide, under optimum conditions, a convenient and unique synthetic route to 1,1-diarylethanes.

In summary, studies of the pyrolyses of benzhydryl oxalates, symmetrical and unsymmetrical, indicate that the initial decomposition step



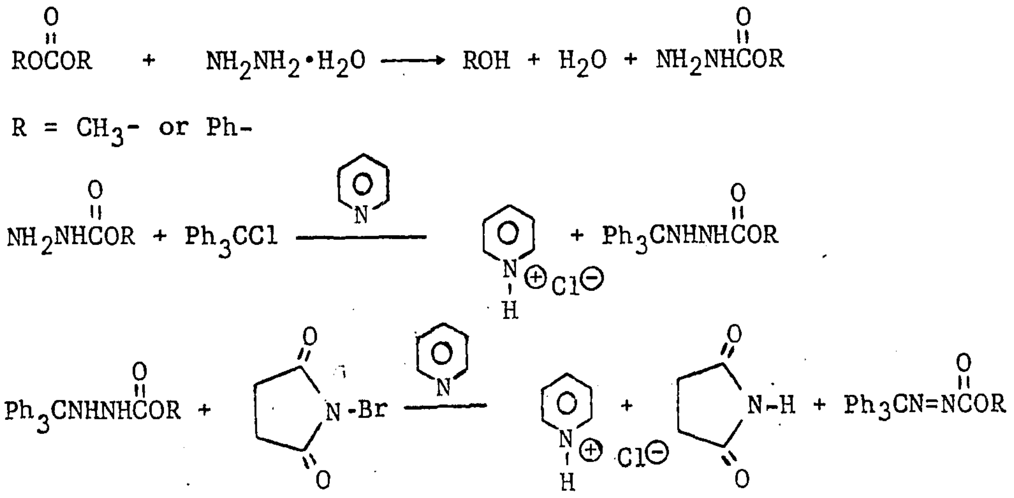
Scheme 7. A possible mechanism for the vapor phase decomposition of methyl benzhydryl oxalate

involves the concerted homolytic cleavage of the alkyl--oxygen bond and the central carbon--carbon bond. The most important finding, however, was the detection of benzyl and benzhydryl diphenylacetates in the pyrolysates of benzyl benzhydryl oxalate and benzhydryl oxalate, respectively. These products can be formed only if the existence of the benzoxycarbonyl and the benzhydroxycarbonyl radicals is allowed. Although the results of labelling experiments show that the major source of these ester products is from an intramolecular recombination of radicals, apparently a small portion of these radicals can escape from the solvent cage to react intermolecularly. From pyrolysis of methyl benzhydryl oxalate in the gas phase it is seen that decarbonylation of the methoxycarbonyl radical is favored at 400° but at higher temperatures decarboxylation becomes the favored process.

Thermal Decomposition of Tritylazocarboxylates

Just as phenylazotrityl heated at 40 - 70° in solution has proved to be a convenient source for phenyl radicals (21, 26, 76), tritylazocarboxylate esters appear to be an ideal system for the generation of alkoxycarbonyl (or aryloxycarbonyl) radicals under mild conditions in order to study the properties of this unusual class of radicals. The trityl-carbon--azo-nitrogen bond should be easily cleaved at low temperatures to produce a stable trityl radical, and a nitrogen molecule should be quickly and perhaps simultaneously lost, leaving only the alkoxycarbonyl radical.

The synthetic route to methyl and phenyl tritylazocarboxylate involves three steps from commercially available starting materials and is outlined in Scheme 8. The overall yield for methyl tritylazocarboxylate was 65%; for phenyl tritylazocarboxylate the overall yield was 32%.



Scheme 8. Synthesis of tritylazocarboxylates

During the decomposition of methyl tritylazocarboxylate in benzene at 60° the evolved gas was collected and analyzed for carbon dioxide and carbon monoxide. Conventional gas analysis (31) detected the presence of no carbon dioxide. Using the ideal gas law pV = nRT and the data in Table 26 a maximum of 2.1 mole % of carbon monoxide can be present. The remainder of the evolved gas was assumed to be nitrogen, an expected product of this decomposition.

The major nonvolatile products arising from the decomposition of methyl tritylazocarboxylate in benzene at 60° under a nitrogen atmosphere were separated by thick layer chromatography on silica gel. The products identified and their yields are presented in Table 6. Also

Table 6. Decomposition products from methyl tritylazocarboxylate

Compound	Moles/mole ester Run 1[a]	Run 2[b]	Run 3[c]
Triphenylmethane	0.21	0.20	0.20
Methyl triphenylacetate	0.24	0.26	0.28
Methyl 4-benzhydrylbenzoate	0.11	0.18	0.14
Methyl 4-carbomethoxytriphenylacetate	0.065	0.035	0.036

[a] Isolated yields from decomposition in benzene; original amount of ester--12.1 mmole.

[b] Decomposed in benzene and analyzed by glpc using benzil as an internal standard; original amount of ester--0.0606 mmole.

[c] Decomposed in cumene and analyzed by glpc using benzil as an internal standard; original amount of ester--0.0681 mmole.

presented in Table 6 are the yields of the major products of the decomposition in benzene and cumene as calculated from the glpc data in Table 27. No measurable quantities of methyl formate, methyl benzoate, methyl oxalate, methyl carbonate, or methyl 2-phenylisobutyrate were ever found.

A crude rate constant for the decomposition of methyl tritylazocarboxylate in benzene at 60° was calculated from the data in Table 25 to be $5.7\ (10)^{-4}$/sec; the half life for this decomposition is ~20 min.

The gas collected during the decomposition of phenyl tritylazocarboxylate in benzene at 75° was analyzed for carbon dioxide and carbon monoxide by gas absorption analysis (31). No carbon dioxide was collected. A maximum yield of 2.2 mole % of carbon monoxide was calculated from the ideal gas law $pV = nRT$ and the data in Table 28. The remainder of the sample analyzed was assumed to be nitrogen, an expected product of the decomposition.

The major nonvolatile decomposition products from phenyl tritylazocarboxylate in benzene at 75° under a nitrogen atmosphere were separated by thick layer chromatography on silica gel. The yields of products which were isolated and identified are presented in Table 7. No measurable quantities of phenyl formate, phenyl benzoate, phenyl oxalate, or phenyl carbonate were noted.

The decompositions of methyl and phenyl tritylazocarboxylates are occurring via a radical path; this was confirmed by the qualitative detection of the presence of trityl radicals in the esr spectra of the crude reaction products.

Table 7. Decomposition products from phenyl tritylazocarboxylate in benzene at 75°

Compound	Moles/mole ester[a]
Triphenylmethane	0.18
Phenyl triphenylacetate	0.11
Phenyl 4-benzhydrylbenzoate	0.16
Mixture[b]	0.11
4,4'-Dicarbophenoxytriphenylmethane	0.032

[a] Isolated yields from 11.6 mmole of ester.

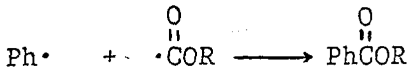
[b] Mixture contained phenyl triphenylacetate and phenyl 4-benzhydrylbenzoate.

Although more than 95% of the theoretical amount of nitrogen was eliminated from both tritylazocarboxylates in benzene in about 3 hr, no evidence for decarboxylation of the methoxycarbonyl or phenoxycarbonyl radicals, indicated by the presence of carbon dioxide, was found, and at best only a small amount (2-3 mole %) of decarbonylation, indicated by the presence of carbon monoxide, could have occurred. Most assuredly, then, the decomposition of these esters at 60 - 75° produced large numbers of methoxycarbonyl and phenoxycarbonyl radicals, and these radicals must have attacked something in the reaction medium.

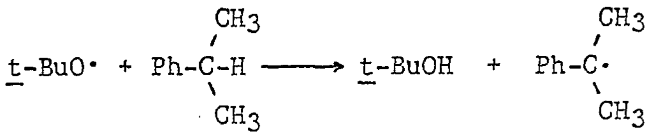
Since there is so much solvent around, the solvent is a likely choice for attack by these radicals. Indeed, Bartlett and Pincock (11) observed reaction by ethoxycarbonyl and benzoxycarbonyl radicals with benzene to yield ethyl and benzyl benzoates and with cumene to produce ethyl and benzyl 2-phenylisobutyrates and abstraction of a hydrogen of cumene to give ethyl and benzyl formates; Pryor (76) describes the addition of radicals into aromatic systems such as benzene. In our decomposition experiments no measurable amounts of benzoates, formates, or 2-phenylisobutyrates were detected; attack by methoxycarbonyl or phenoxycarbonyl radicals on molecules of solvent to produce simple products does not occur.

The obvious discrepancy between Bartlett's results and ours can be rationalized in the following way (equations 11-15).

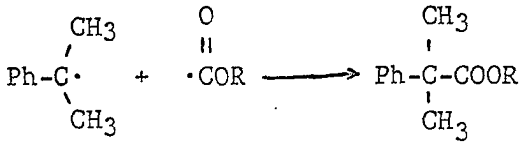
(11) $\underline{t}\text{-BuO}\cdot + \text{Ph-H} \longrightarrow \underline{t}\text{-BuOH} + \text{Ph}\cdot$

(12)


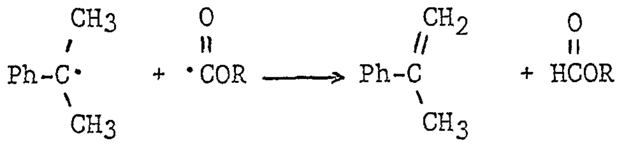
$$\text{Ph}\cdot + \cdot\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{OR} \longrightarrow \text{Ph}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{OR}$$

(13)


$$\underline{t}\text{-BuO}\cdot + \text{Ph-C}(\text{CH}_3)_2\text{-H} \longrightarrow \underline{t}\text{-BuOH} + \text{Ph-}\dot{\text{C}}(\text{CH}_3)_2$$

(14)


$$\text{Ph-}\dot{\text{C}}(\text{CH}_3)_2 + \cdot\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{OR} \longrightarrow \text{Ph-C}(\text{CH}_3)_2\text{-COOR}$$

(15)


$$\text{Ph-}\dot{\text{C}}(\text{CH}_3)_2 + \cdot\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{OR} \longrightarrow \text{Ph-C}(=\text{CH}_2)\text{CH}_3 + \text{H}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{OR}$$

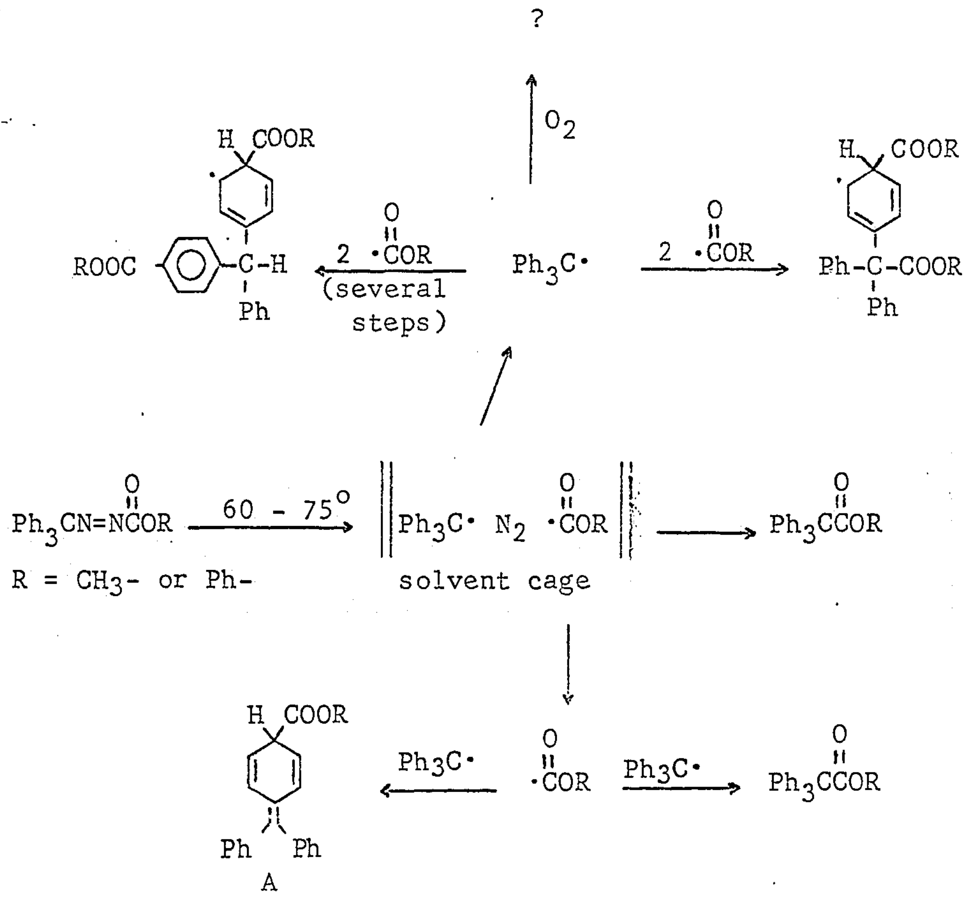
In Bartlett's decomposition of ethyl (and benzyl) t-butylperoxyoxalates, the very "hot" t-butoxy radical as well as the "cool" alkoxycarbonyl radical is produced; in our tritylazocarboxylate decompositions the other fragment produced besides the alkoxycarbonyl (or aryloxycarbonyl) radical is the very "cool" trityl radical. We propose that it is the "hot" t-butoxy radical which initiates reactions with solvent to produce radical species which can couple with the alkoxycarbonyl radical to form such products as alkyl benzoates and alkyl 2-phenylisobutyrates or from which a hydrogen atom can be abstracted producing alkyl formates. Trityl radicals would not attack the solvent generating these solvent related radical species.

Coupling of two methoxycarbonyl or two phenoxycarbonyl radicals to produce an oxalate is a possible reaction pathway, but no oxalates were noted among the decomposition products; coupling of the radicals does not seem to be an important process in these decompositions.

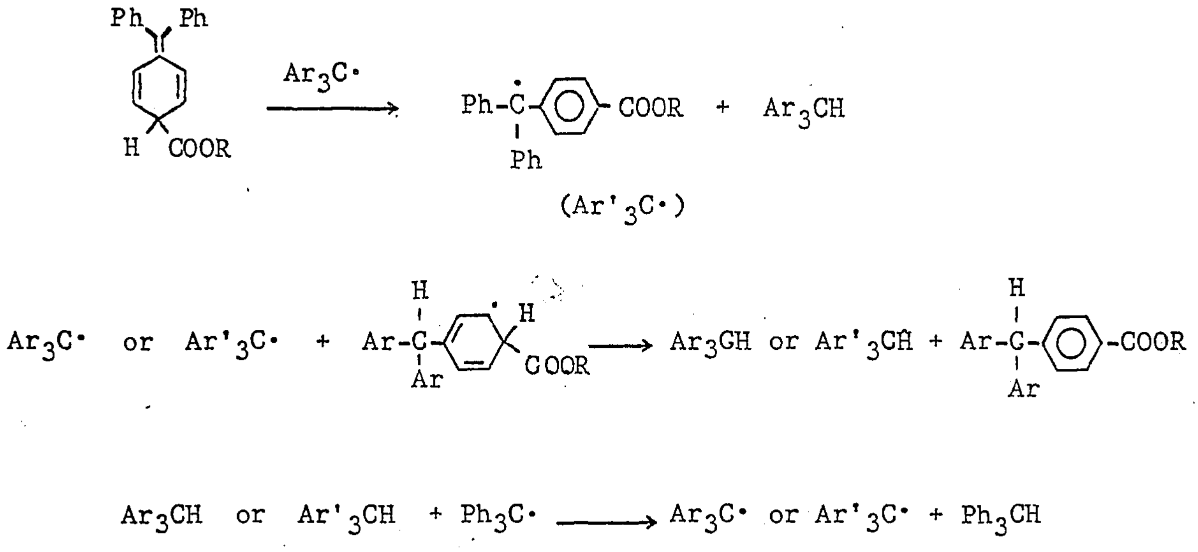
The only other mode of reaction available for the radicals is coupling with the trityl radicals. As can be seen in Tables 6 and 7, the major isolable products reflect such a coupling process. Just how much of the triphenylacetate is a result of cage recombination of radicals and how much is formed by an intermolecular coupling is not known. Formation of the other products, 4-benzhydrylbenzoates and the diester compounds, can occur only if the methoxycarbonyl and phenoxycarbonyl radicals survive long enough to choose their point of attack on the trityl or substituted trityl radical. Indeed, the diester products can arise only if the methoxycarbonyl and phenoxycarbonyl radicals escape from the solvent cage and are free in solution.

On the basis of the products isolated and identified, 63-68% of the trityl groups and 42-48% of the methoxycarbonyl groups from the methyl tritylazocarboxylate decomposition and 60% of the trityl groups and 42% of the phenoxycarbonyl groups from the phenyl tritylazocarboxylate decomposition can be directly accounted for. In addition, a total of five other compounds (0.1-0.3 gm each) from both decompositions containing trityl and/or alkoxycarbonyl groups were isolated but could not be conclusively identified. The number and nature of the decomposition products was further complicated by the reaction of oxygen with the excess trityl radicals after decomposition of the tritylazocarboxylate was complete, so that at least 20 distinct bands for each decomposition could be seen on the thick layer chromatography plates. Although complete analysis of the decomposition products is hopeless, the major products have been identified, and from the information in hand the following schemes (Schemes 9 and 10) were constructed to give at least a partial picture of the mechanism of the decomposition of tritylazocarboxylate esters.

The formation of considerable amounts of triphenylmethane in these decompositions implies that the trityl radical is abstracting a hydrogen atom from another triarylmethane or from some other radical source. Three such sources would be the radical precursors to methyl 4-carbomethoxytriphenylacetate and 4,4'-dicarbophenoxytriphenylmethane and intermediate A (Scheme 9) leading to the 4-benzhydrylbenzoates. Other sources could be among the unidentified products mentioned above. The hydrogen-abstraction process is described in Scheme 10. Formation of such di-, tri-, or polyesters on one trityl group would create the excess of trityl radicals observed by esr spectroscopy in both decompositions.



Scheme 9. Partial mechanism of the decomposition of tritylazocarboxylate esters



Scheme 10. Possible hydrogen-abstraction processes in the decomposition of tritylazocarboxylates

At this point a brief recapitulation of the findings about alkoxycarbonyl radicals is in order. Confirmation of the existence of the alkoxycarbonyl radical as a distinct entity was given by the decomposition experiments on benzhydryl oxalates, and a convenient method for generating alkoxycarbonyl radicals from tritylazocarboxylate esters was discovered. Compared to the related alkylcarboxy radicals which have proved to be very unstable, alkoxycarbonyl radicals are relatively stable species. These radicals can escape from a solvent cage and before decarboxylation or decarbonylation can attack radical species in solution other than themselves; alkoxycarbonyl radicals are unreactive radicals because aromatic solvents such as benzene are not attacked and active hydrogen-atom donating solvents such as cumene do not act as hydrogen-atom donors. At 400° methoxycarbonyl radicals tend to decarbonylate; at higher temperatures decarboxylation predominates.

Pyrolysis of Triphenylacetates

Initially it was hoped that esters of triphenylacetic acid having no β hydrogens might provide a source of alkoxycarbonyl radicals. However, as the discussion will presently show, this was not the case. Instead, some unusual and unexpected results were obtained.

Following the literature preparation for these esters (73), 70-80% yields of the methyl and phenyl esters of triphenylacetic acid were isolated by refluxing triphenylacetyl chloride in the corresponding alcohol, but the maximum yield of the benzyl ester[1] was only ~50% by this method. During the refluxing period for the benzyl ester considerable water was inexplicably formed; also a small amount of triphenylacetic acid was recovered.

Ideally, the solvent of choice for the examination of thermal decompositions of molecules at high temperatures (200 - 400°) in tubes sealed under vacuum should have these properties: high boiling point (> 200°) at 1 atmosphere to prevent excessive pressure buildup under these extreme conditions, chemical inertness to minimize attack on the solvent by the thermally decomposing molecules, and thermal stability to eliminate undesirable side reactions initiated by solvent molecules. It is probably impossible to find an aromatic solvent which is totally resistant to attack by the free radicals (76) formed at these temper-

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[1] Yield of benzyl ester was not reported by Norris and Cresswell.

atures, and indeed our results can only be explained if attack on solvent molecules by the molecular fragments present is allowed (Schemes 11 and 12 and equation 17).

Samples of biphenyl, phenyl ether, 1,3,5-triisopropylbenzene, naphthalene, and 1-chloronaphthalene were degassed and sealed under vacuum and were examined for their suitability in these respects.

All of these compounds had boiling points $>200^{\circ}$ at 1 atmosphere, but they differed in their thermal stabilities. Comparison of samples heated in an aluminum block constant temperature apparatus (Figure 1) at 350° for 30 days with unpyrolyzed samples by glpc analysis showed that biphenyl, phenyl ether, and naphthalene experienced no detectable decomposition while 1-chloronaphthalene and 1,3,5-triisopropylbenzene did undergo some decomposition (not quantitatively determined). Although 1,3,5-triisopropylbenzene did experience some auto-decomposition, it could still prove useful as a radical trap.

Norris and Cresswell (73) thermally decomposed benzyl triphenylacetate by rapidly heating the ester to its boiling point. The major nonvolatile product identified was triphenylmethane; the gaseous products contained carbon dioxide (37%) and carbon monoxide (42.4%), the residual gas being air. Because of the high yield of carbon monoxide, benzaldehyde was postulated, but not demonstrated, to be a pyrolysis product.

In our experiments at 350° in biphenyl, phenyl ether, or 1,3,5-triisopropylbenzene as a solvent, the nonvolatile products, the yields of which are presented in Tables 8, 9, and 10, included the startling find of benzophenone and diphenylmethane as major products. Not even a trace of benzaldehyde was found. Benzyl trityl ether, trityl phenylacetate, and 1,1,1,2-tetraphenylethane, which could conceivably be products of this pyrolysis, were not detected, nor did any starting ester remain.

Table 8. Decomposition products[a] of benzyl triphenylacetate in biphenyl at 350°

Compound	Moles/mole ester Run 1	Run 2	Run 3	Run 4
Original ester[b]	1.00	1.00	1.00	1.00
Toluene	0.252[c]	0.201	0.239	0.231
Diphenylmethane	0.533[c]	0.513	0.532	0.562
Benzophenone	0.510	0.568	0.589	0.598
Triphenylmethane	0.360	0.354	0.384	0.376
Unknown[d,e]	0.09	0.09	0.09	0.09

[a] Products were identified by peak enhancement (nmr and glpc).

[b] Amount of ester pyrolyzed: Run 1--0.149 mmole; Run 2--0.0925 mmole; Run 3--0.101 mmole; Run 4--0.0952 mmole.

[c] Calculated from nmr integration data by multiplying the ratio of the nmr peak areas $\frac{\text{Area X}}{\text{Area Y}}$ times the number of mmole of Y as determined by glpc analysis.

[d] May be tritanol, tetraphenylmethane, or 9-phenylfluorene.

[e] Yields were calculated by assuming the same thermal conductivity ratio for unknown as for triphenylmethane.

Table 9. Decomposition products[a] of benzyl triphenylacetate in phenyl ether at 350°

Compound	Run 5	Run 6	Run 7	Run 8
	Moles/mole ester			
Original ester[b]	1.00	1.00	1.00	1.00
Toluene	0.202	--	0.148	0.342
Unknown A	Not calculated			
Diphenylmethane[c]	0.536	0.31	0.36	0.25
Benzophenone	0.607	0.524	0.520	0.374
Triphenylmethane	0.439	0.398	0.413	0.510
Unknown B[d,e]	0.07	0.09	0.07	0.09

[a] Products were identified by peak enhancement (nmr and glpc).

[b] Amount of ester pyrolyzed: Run 5--0.0860 mmole; Run 6--0.105 mmole; Run 7--0.121 mmole; Run--0.0947 mmole.

[c] Calculated from nmr integration data by multiplying the ratio of the nmr peak areas $\frac{\text{Area X}}{\text{Area Y}}$ times the number of mmole of Y as determined by glpc analysis.

[d] May be tritanol, tetraphenylmethane, or 9-phenylfluorene.

[e] Yields were calculated by assuming the same thermal conductivity ratio for unknown as for triphenylmethane.

Table 10. Decomposition products[a] of benzyl triphenylacetate in 1,3,5-triisopropylbenzene at 350°

Compound	Moles/mole ester		
	Run 9	Run 10[b]	Run 11
Original ester[c]	1.00	1.00	1.00
Toluene	--	0.459	0.521
Diphenylmethane	--	0.654	0.609
Benzophenone	0.270	0.353	0.302
Triphenylmethane	0.468	0.600	0.562

[a] Products were identified by peak enhancement (nmr and glpc).

[b] Not all of the standard, benzil, dissolved; therefore, results may be high.

[c] Amount of ester pyrolyzed: Run 9--0.132 mmole; Run 10--0.0958 mmole; Run 11--0.0868 mmole.

Using the thermal conductivity ratio data of the reference solutions in Table 16 and the peak areas of the products in the pyrolysates in Tables 29-32, and assuming a constant value of the thermal conductivity ratio over the range of concentrations investigated, the yields of products can be calculated as in equation 16:

$$\text{(16)}\qquad \text{mmole of R} = \frac{\left(\dfrac{\text{area benzil}}{\text{area R}}\right)_{\text{ref}} \; (\text{mmole benzil})_{\text{pyr}}}{\left(\dfrac{\text{mmole benzil}}{\text{mmole R}}\right)_{\text{ref}} \; \left(\dfrac{\text{area benzil}}{\text{area R}}\right)_{\text{pyr}}}$$

The gases produced during the pyrolysis of benzyl triphenylacetate in phenyl ether at 350° were collected and analyzed for carbon dioxide and carbon monoxide. Substituting the data in Table 33 into the ideal gas law expression, pV = nRT, the yields presented in Table 11 were obtained.

Table 11. Gaseous products from the pyrolysis of benzyl triphenylacetate in phenyl ether at 350°

Compound	Moles/mole ester	
	Run 1	Run 2
Original ester[a]	1.00	1.00
Carbon dioxide	0.208[b]	0.170
Carbon monoxide	0.534	0.534

[a] Amount of ester pyrolyzed: Run 1--1.99 mmole; Run 2--2.00 mmole.

[b] Probably too high by ~1 part in 10.

Assuming Beer's law to hold over the range of concentrations examined, absorbance A is proportional to the concentration c (34). In Figure 3 (p. 118) absorbance A is plotted as a function of time t in min for the thermal decomposition of benzyl triphenylacetate (Run 2). The first order rate constant k for this unimolecular process can be evaluated from equation 17 (72); the half life $t_{\frac{1}{2}}$ can be read directly from the Figure. For benzyl triphenylacetate the rate

$$k = \frac{\ln 2}{t_{\frac{1}{2}}} \qquad (17)$$

constant k equals $4.64\ (10)^{-5}$/sec with a 1.4% deviation for 2 runs.

Similarly for the formation of benzophenone the rate constant was found to be 5.50 $(10)^{-5}$/sec with a 5.8% deviation for 2 runs.

Even though benzyl trityl ether and trityl phenylacetate were not detected in the pyrolysates of benzyl triphenylacetate, either or both of them could conceivably be intermediates which subsequently were thermally decomposed. These compounds were, therefore, synthesized and pyrolyzed.

Preparation from tritanol, benzyl alcohol, and a trace of p-toluenesulfonic acid (75) produced a 79% yield of benzyl trityl ether.

Using a method patterned after that of Berlin et al. (16), trityl phenylacetate was prepared in 70% yield from trityl bromide and potassium phenylacetate in benzene. This compound is apparently moisture or air sensitive, and suitable precautions should be taken to prevent exposure to these elements.

The observation that benzyl trityl ether was thermally decomposed into benzaldehyde and triphenylmethane has been made (74). Our product studies in biphenyl at 350° failed to uncover any other products such as benzophenone, diphenylmethane, or toluene. In Table 12 are presented the results of these studies calculated from Tables 34 and 35.

The product studies on the thermal decomposition of trityl phenylacetate in biphenyl at 350° are summarized in Table 13 using the data in Tables 36 and 37.

Very little of the "benzylic" portion of the molecule was accounted for in this study; it seems likely by analogy to work of Berlin and coworkers (15, 17, 18) that phenylacetic acid and/or its anhydride would

Table 12. Decomposition products[a] of benzyl trityl ether in biphenyl at 350°

Compound	Moles/mole ether Run 1	Run 2	Run 3	Run 4
Original ether[b]	1.00	1.00	1.00	1.00
Benzaldehyde	0.637	0.703	0.680	0.558
Triphenylmethane	0.978	0.970	1.00	0.986

[a] Products were identified by peak enhancement (nmr and glpc).

[b] Amount of ether pyrolyzed: Run 1--0.0937 mmole; Run 2--0.101 mmole; Run 3--0.0954 mmole; Run 4--0.107 mmole.

Table 13. Decomposition products[a] of trityl phenylacetate in biphenyl

Compound	Moles/mole ester Run 1[b]	Run 2[c]	Run 3[d]	Run 4[e]
Original ester	1.00	1.00	1.00	1.00
Diphenylmethane	0.156	0.110	0.041	0.038
Benzophenone	0.267	0.244	0.227	0.216
Triphenylmethane	0.475	0.463	0.493	0.528
Unknown A	Not calculated			
Unknown B	Not calculated			

[a] Products were identified by peak enhancement (nmr and glpc).

[b] Heated at 295° for 12 hr; amount of ester pyrolyzed--0.0995 mmole.

[c] Heated at 260° for 62 hr; amount of ester pyrolyzed--0.0986 mmole.

[d] Heated at 235° for 122 hr; amount of ester pyrolyzed--0.0905 mmole.

[e] Heated at 230° for 240 hr; amount of ester pyrolyzed--0.115 mmole.

be major products of this decomposition, but rigorous proof of their presence or absence, being immaterial to the immediate aim of this study, was not undertaken.

Methyl triphenylacetate has been thermally decomposed (73) by heating at its boiling point for an unspecified length of time. The major nonvolatile product was identified as triphenylmethane; the volatile products were also collected and analyzed and found to contain carbon dioxide (12%), carbon monoxide (8%), an unidentified hydrocarbon (18%), and a substance which was readily absorbed in water, presumably formaldehyde (62%).

In our product study a degassed sample of methyl triphenylacetate in phenyl ether was sealed under vacuum and pyrolyzed at 350° for 10 days (5-6 half lives). In Table 14 the yields of the major nonvolatile products detectable by glpc analysis are listed.

Table 14. Decomposition products[a] of methyl triphenylacetate in phenyl ether

Compound	Moles/mole ester
Original ester[b]	1.00
Toluene	0.0726
Benzophenone	0.106
Triphenylmethane	0.555

[a] Products were identified by peak enhancement (nmr and glpc).

[b] Original amount of ester was 0.102 mmole.

From a plot of absorbance A against time t in min for the thermal decomposition of methyl triphenylacetate, the rate constant was calculated to be 4.70 $(10)^{-6}$/sec.

Phenyl triphenylacetate has also been thermally decomposed (2) into phenol and triphenylmethane; no yields or conditions were reported. In phenyl ether at 350° for 10 days we have also found these compounds to be the major nonvolatile products. In Table 15 the yields of these compounds are reported, using the data in Table 39.

Table 15. Decomposition products[a] of phenyl triphenylacetate in phenyl ether at 350°

Compound	Moles/mole ester
Original ester[b]	1.00
Phenol	0.698
Triphenylmethane	0.748

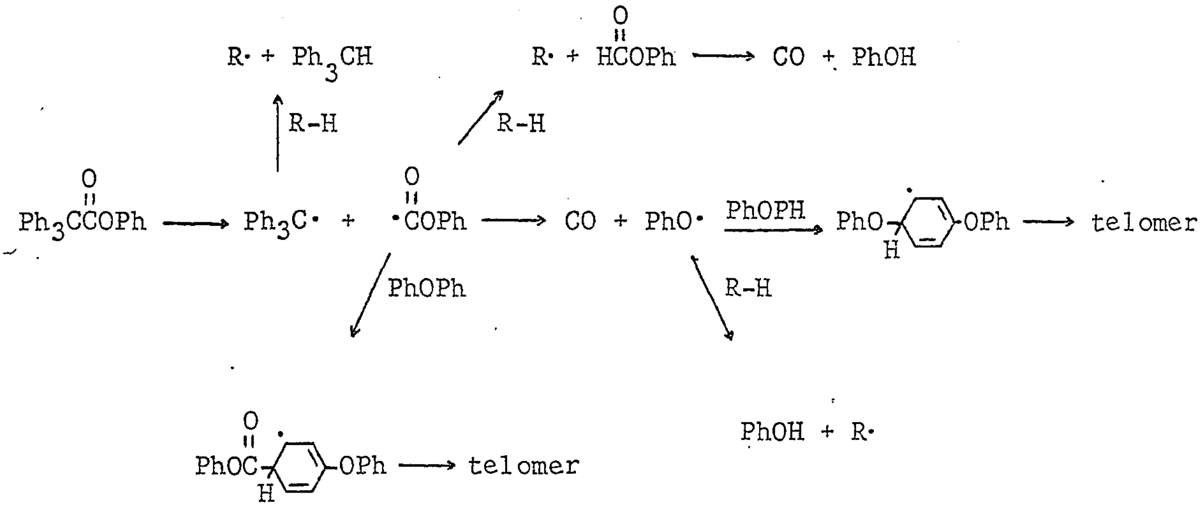
[a] Products were identified by peak enhancement (nmr and glpc).

[b] Amount of ester pyrolyzed was 0.123 mmole.

From a plot of absorbance A versus time t in min, the first order rate constant k for the thermal decomposition of phenyl triphenylacetate can be evaluated and for an average of 2 runs is found to be 3.31 $(10)^{-6}$/sec with a 7.2% deviation for 2 runs.

From the evidence gathered on the pyrolyses of these esters of triphenylacetic acid, the following generalization can be made. Whatever the exact nature of the initial transition state or intermediate in these pyrolytic decompositions is, it is clear that the phenyl triphenylacetate system follows only one pathway to products--each decomposing molecule yields one trityl radical which ultimately abstracts a hydrogen atom from a hydrogen-donating substrate, presumably a solvent adduct, to form triphenylmethane, and most of the decomposing molecules decarbonylate yielding carbon monoxide and the phenoxy radical which can abstract a hydrogen atom, producing phenol. From these data it cannot be determined whether phenoxy radicals or phenoxycarbonyl radicals add into the solvent to produce active hydrogen donating species, probably telomeric in nature. Phenyl formate could be an intermediate; this compound has been shown to decompose (65) into carbon monoxide and phenol. A likely mechanism for phenyl triphenylacetate decomposition would be as in Scheme 11.

For the other two systems at least two pathways to products seem to be available--one mode of decomposition, presumably by a mechanism similar to that in Scheme 11, leads to the trityl radical which abstracts a hydrogen from a hydrogen-donating source to form triphenylmethane and to the alkoxycarbonyl radical which either adds into the solvent to produce active hydrogen-donating species, probably telomeric, or decarboxylates to yield an alkyl radical which can abstract a hydrogen to form the corresponding arylalkane; the second mode of decomposition involves transfer of a phenyl group from the trityl portion of the ester to the other alkyl portion to form the corresponding arylalkane probably simultaneously with formation of an intermediate which readily leads to benzophenone and carbon monoxide.

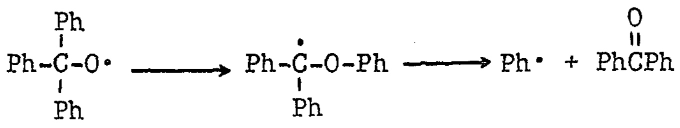


Scheme 11. Mechanism of phenyl triphenylacetate decomposition

The mode of benzophenone--arylalkane formation is operating in both the methyl triphenylacetate and benzyl triphenylacetate decompositions, but from the benzyl ester much more benzophenone and diphenylmethane are formed at a much more rapid rate, a rate which is, within experimental error, the same as for the overall decomposition of the benzyl ester and which is 10 times faster than the rate of decomposition of the methyl ester. This rate difference may reflect a difference in the stabilities of the methyl and benzyl cations or radicals.

The fundamental question raised by the results of these pyrolyses is: what mechanism of decomposition can be devised which will adequately accommodate the totally unexpected observation of benzophenone and arylalkane formation? Any mechanism which is postulated must be able to explain the formation of benzophenone and diphenylmethane in approximately equal amounts.

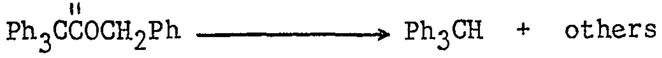
If an intermediate derived from benzyl triphenylacetate could provide a source of tritoxy radicals, then a pathway to benzophenone formation (38, 15) would be available (equation 18).

(18) 

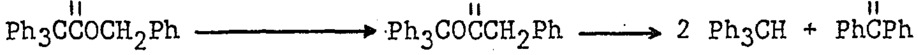
$$\mathrm{Ph{-}\overset{Ph}{\underset{Ph}{C}}{-}O\cdot} \longrightarrow \mathrm{Ph{-}\overset{\bullet}{\underset{Ph}{C}}{-}O{-}Ph} \longrightarrow \mathrm{Ph\cdot} + \mathrm{Ph\overset{O}{\overset{\|}{C}}Ph}$$

Two such possible intermediates were investigated. Pyrolysis of benzyl trityl ether gave rise to only benzaldehyde and triphenylmethane; no benzophenone was detected. This compound is thus eliminated from consideration as a precursor to benzophenone.

Trityl phenylacetate pyrolysis did indeed yield benzophenone and must be a source of the tritoxy radical. If it is assumed that some benzyl triphenylacetate molecules are inverted (40) to trityl phenylacetate before pyrolysis while all other molecules of benzyl triphenylacetate are decomposed to yield triphenylmethane and that trityl phenylacetate is the only source of benzophenone arising from pyrolysis of benzyl triphenylacetate, then equations 19 and 20 represent what is occurring.

(19) 

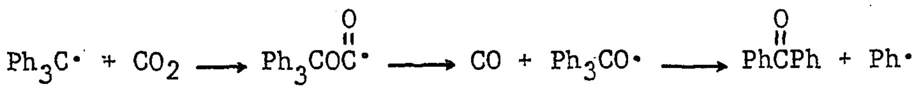
$$\mathrm{Ph_3\overset{O}{\overset{\|}{C}}OCH_2Ph} \longrightarrow \mathrm{Ph_3CH} + \text{others}$$

(20) 

$$\mathrm{Ph_3\overset{O}{\overset{\|}{C}}OCH_2Ph} \longrightarrow \mathrm{Ph_3CO\overset{O}{\overset{\|}{C}}CH_2Ph} \longrightarrow 2\ \mathrm{Ph_3CH} + \mathrm{Ph\overset{O}{\overset{\|}{C}}Ph}$$

Experimentally, trityl phenylacetate yielded roughly 2 parts of triphenylmethane to 1 part of benzophenone; adding to this the 1 part of triphenylmethane expected from direct decomposition of benzyl triphenylacetate (equation 14), one would predict to find in the pyrolysate of benzyl triphenylacetate 3 parts of triphenylmethane to 1 part of benzophenone. In actuality, the pyrolysate of benzyl triphenylacetate contained about 1.5 parts of benzophenone to 1 part of triphenylmethane. The conclusion is, then, that trityl phenylacetate is not the precursor to benzophenone formation in the pyrolysis of benzyl triphenylacetate.

Another conceivable source of tritoxy radicals and hence benzophenone is decarbonylation of tritoxycarbonyl radicals resulting from reaction of trityl radicals with carbon dioxide (equation 21). However, this pathway seems unlikely in view of the small concentration of carbon

(21)


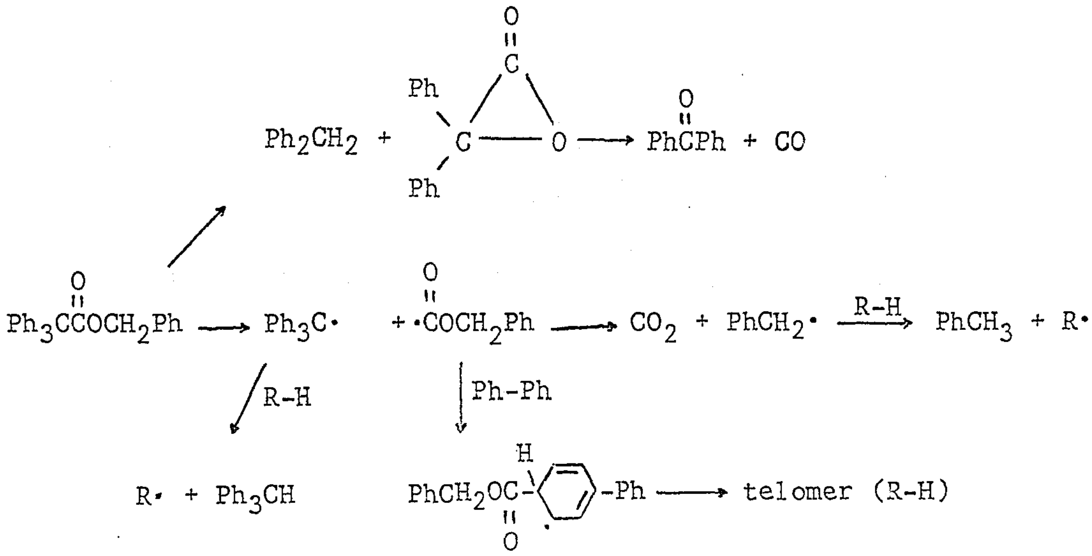
$$Ph_3C\cdot + CO_2 \longrightarrow Ph_3CO\overset{\overset{O}{\|}}{C}\cdot \longrightarrow CO + Ph_3CO\cdot \longrightarrow Ph\overset{\overset{O}{\|}}{C}Ph + Ph\cdot$$

dioxide at any given time and the lack of precedent in the literature for such radical additions to carbon dioxide.

On the basis of the data now in hand, the following mechanism (Scheme 12) is proposed.

In order to form diphenylmethane, benzophenone, and carbon monoxide in equal quantities from benzyl triphenylacetate, a 1,4-phenyl migration from the triphenylmethyl group to the benzyl group must occur. Thermally induced 1,4-phenyl migrations are apparently not known, but several examples of 1,4-phenyl migration to $n \rightarrow \pi^*$ excited carbonyl groups have been observed (25b, 41b, 80b, 92), and one example of a 1,4-phenyl migration induced by electron impact is known.[1]

Invocation of α-lactone intermediates, especially in radical reactions, is quite rare, but Bartlett and Gortler (9) seem to have trapped diphenyl α-lactone with methanol in their decomposition study of di-*t*-butyl diperoxydiphenylmalonate.



Scheme 12. Mechanism of decomposition of benzyl triphenylacetate

Under their conditions most of the α-lactone apparently polymerized, but a sizeable quantity (0.15 mole/mole of perester) of benzophenone was found. If diphenyl α-lactone is allowed as an intermediate, then in the decomposition of *t*-butyl peroxytriphenylacetate (63) benzophenone formation (0.15-0.20 mole/mole of perester), which was not adequately ex-

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[1] O. L. Chapman, T. H. Kinstle, and M. T. Sung, Ames, Iowa. Private communication. 1967.

plained, can be readily rationalized.

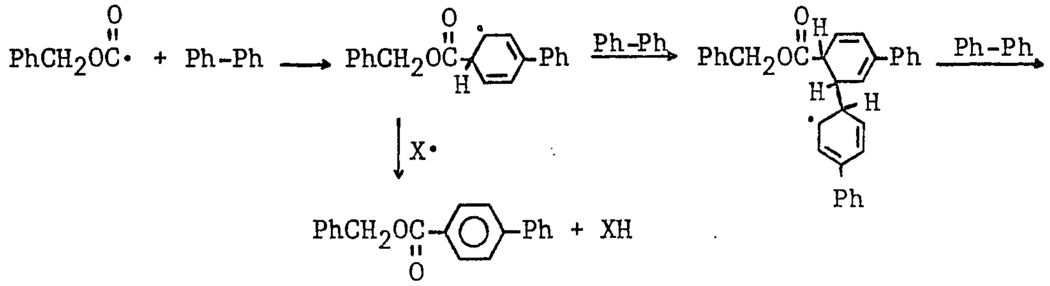
Although diphenyl α-lactone may have an appreciable lifetime, this highly strained compound would not be expected to survive very long at 350°; benzophenone and carbon monoxide are very reasonable decomposition products.

An attempt was made to trap the α-lactone by pyrolyzing benzyl triphenylacetate in the presence of methanol (9); the product mixture did not appreciably differ from the pyrolysate with no methanol, most of the methanol was recovered, and no evidence for the expected products of trapping, the methyl ether of benzilic acid or its decarboxylated derivative, methyl benzhydryl ether, was found.

Assuming the competing routes to products in Scheme 12 to be the major decomposition pathways for benzyl (and methyl) triphenylacetate, one would expect to observe equal yields of benzophenone, diphenylmethane, and carbon monoxide; in Tables 8, 9, and 11 are recorded yields of ~0.55 mole, ~0.54 mole, and 0.53 mole, respectively. The amount of toluene formed should equal the amount of carbon dioxide evolved, and the missing benzyl portion should equal the missing ester groups (-COO-) (this amount of benzoxycarbonyl groups have added into the solvent). From the data ~0.20 mole of toluene and 0.17 mole of carbon dioxide were found; the missing benzyl portion is ~0.26 mole (1.00 mole of ester minus 0.54 mole of diphenylmethane minus 0.20 mole of toluene) while the missing ester groups amount to ~0.30 mole (1.00 mole of ester minus 0.53 mole of carbon monoxide minus 0.17 mole of carbon dioxide). The fate of the trityl portion of the ester should be accounted for by the sum of the benzophenone and triphenylmethane yields; this sum is ~0.92 mole/mole of ester. An unknown which has about the same retention time as triphenylmethane presumably contains a trityl group and would account for the remainder of the trityl groups (~ 0.09 mole).

A cursory glance at, for example, Table 8 reveals that far more hydrogens are present in the products than can possibly have come from the ester. The only reasonable source for these extra hydrogens is the solvent. Radical addition into aromatic solvents is well documented (76, 79); addition of a benzoxycarbonyl radical into biphenyl (Scheme 12 and equation 22) produces a species which has a readily abstractable hydrogen. However, rather than lose a hydrogen, it is quite likely that this species attacks another molecule or two of solvent, producing a species having several reactive hydrogen atoms available for abstraction.

(22)



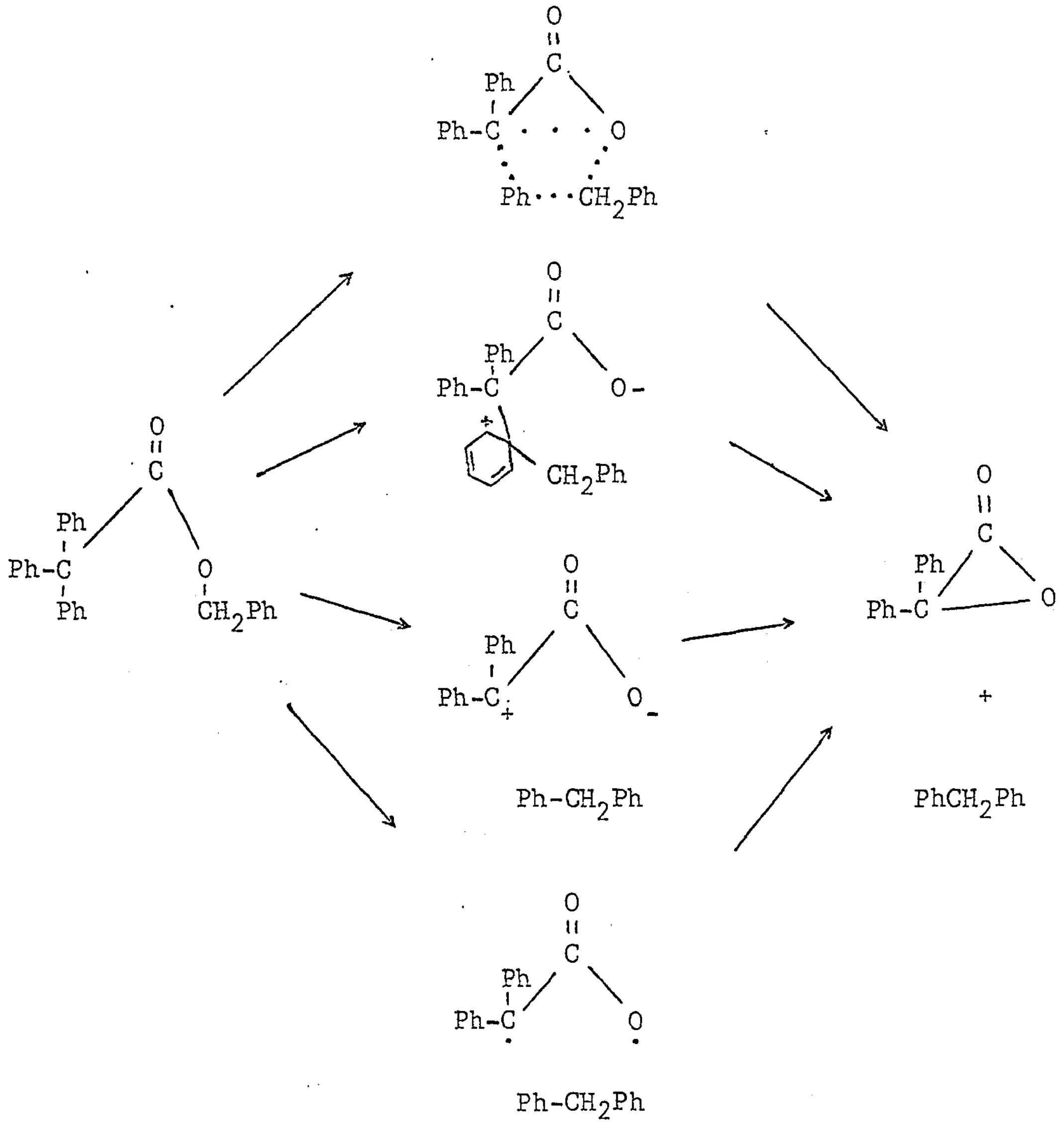
These solvent adducts would undoubtedly escape detection by glpc and may or may not be seen in the nmr spectrum.

A complete rationale for the decomposition of benzyl triphenylacetate in a solvent with hydrogens readily available for abstraction, i.e., 1,3,5-triisopropylbenzene, cannot be made at this time. However, it can be noted that the path leading to benzophenone was not totally disrupted, since ~0.30 mole of benzophenone/mole of ester was found; complete disruption of this route would not be expected if diphenyl α-lactone were an intermediate in this decomposition. An equivalent yield of diphenylmethane would be expected; instead, almost double that yield (~0.62 mole) was found. This finding is a mystery, but perhaps the glpc peak measured was due not only to diphenylmethane but also to a solvent-related product, since other such solvent-related peaks were observed to have about the same retention times.

If the α-lactone is indeed an intermediate, as it seems to be, four distinct pathways to this intermediate are conceivable: a process involving a cyclic, concerted transition state, a mechanism involving phenyl bridging in a zwitterionic intermediate, a mechanism involving heterolytic cleavage of bonds, and a diradical mechanism involving homolytic cleavage of bonds (Scheme 13).

The experiments performed in this study do not allow a distinction to be made among the available routes leading to the diphenyl α-lactone.

In this study of pyrolyses of triphenylacetates the most startling result is the observation that equal amounts of benzophenone, diphenylmethane, and carbon monoxide are formed from benzyl triphenylacetate. Formally, a phenyl migration from the triphenylmethyl group to the benzyl group must occur to give rise to these products; apparently, this decomposition requires the intervention of a short-lived diphenyl α-lactone species.



Scheme 13. Possible pathways leading to diphenyl α-lactone and diphenylmethane

EXPERIMENTAL

All melting points and boiling points are uncorrected and are given in degrees Centigrade. Pressure is given in millimeters of mercury. The melting points were determined on a Thomas-Hoover Unimelt Melting Point Apparatus. The infrared (ir) spectra were measured on a Perkin-Elmer Model 21 instrument, and characteristic peaks are given in reciprocal centimeters (cm^{-1}). Peak intensities are designated as broad (b), weak (w), moderate (m), strong (s), and very strong (vs). In obtaining all of the ir spectra chloroform was used as the solvent unless otherwise noted; spectra were thus limited to the range 5000-830 cm^{-1}. All nuclear magnetic resonance (nmr) spectra were measured on a Varian A-60 spectrometer using, unless otherwise indicated, deuteriochloroform as solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts are measured in terms of δ-values (TMS absorption is at 0 δ). Following the chemical shift value in parentheses, absorption multiplicity, indicated by singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (b), and the proton ratio are given. Mass spectral data were obtained with an Atlas CH-4 Mass Spectrometer, and the important mass/charge ratio numbers are reported. Electron spin resonance (esr) spectra were measured using a Varian Associates V-4500 spectrometer with a 100 kcps field modulation and with a 9 inch magnet, regulated by a Fieldial control. All gas-liquid phase chromatography (glpc) analyses were done with an Aerograph Model 200 instrument using 6 ft aluminum columns packed with 15% SE-30 liquid phase on 60/80 mesh Chromosorb P.

Instrument conditions were flow rate ~60 ml of helium per min, column temperature programmed from ~125° to 265°, injector temperature 225° to 270°, and detector temperature 300° to 315°. Peak areas of the glpc traces were measured with a planimeter. Elemental analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Michigan, or M-H-W Laboratories, Garden City, Michigan.

Syntheses

The method for the preparation of benzhydryl oxalates was patterned after the method of Lespagnol (59).

Benzhydryl oxalate

Two hr were required to azeotrope the water contained in 5.77 gm (45.8 mmole) of oxalic acid dihydrate (Baker Chemical Co.) into a Dean-Stark trap with 100 ml of benzene. Then 16.22 gm (88.1 mmole) of benzhydrol (Matheson Coleman and Bell) and ~50 mg of *p*-toluenesulfonic acid were added, and the mixture was allowed to reflux for 20 hr in order to remove the water formed during the esterification as an azeotrope. After washing with an equal volume of water, an equal volume of saturated sodium bicarbonate, and again an equal volume of water the benzene layer was dried over magnesium sulfate. The benzene was stripped off by rotary evaporation at reduced pressure, and crystals appeared. Recrystallized from hexane was 16.39 gm (90%) of benzhydryl oxalate (mp 141 - 142°; lit (62) mp 142 - 143°). Nmr δ 7.32 (s, 20) and 6.96 (s, 2); ir 1767 (vs), 1747 (vs), 1600 (w), 1450 (m), 1290 (m), 1160 (vs), and 940 cm^{-1} (m).

Benzhydryl oxalate-α-d_1

The water contained in 0.64 gm (5.08 mmole) of oxalic acid dihydrate (Baker Chemical Co.) was removed as an azeotrope with 20 ml of benzene into a Dean-Stark trap in 12 hr. After addition of 1.86 gm (10.1 mmole) of benzhydrol-α-d_1 prepared by E. Geels and approximately 15 mg of p-toluenesulfonic acid, the water produced in the course of esterification was removed as an azeotrope of benzene in 6.5 hr. The reaction mixture was then washed twice with equal volumes of saturated sodium bicarbonate and twice with distilled water. The benzene layer was dried over magnesium sulfate overnight. After filtering the benzene was removed at reduced pressure by rotary evaporator. The crystalline residue was taken up in a minimum of dichloromethane and was recrystallized from hexane to yield 1.71 gm (80.3%) of benzyhydryl oxalate-α-d_1 (mp 145 - 147°). Nmr δ 7.22 (d). No trace of benzhydryl proton at 6.96δ is apparent. Ir 1770 (vs), 1740 (vs), 1500 (m), 1450 (m), 1357 (m), 1330 (m), 1160 (vs), 1080 (m), 1017 (m), 1002 (m), 934 (m), and 905 cm^{-1} (m).

Benzhydryl ether

When 5.0 gm of benzhydrol (Matheson Coleman and Bell) and 100 ml of 3.5 N hydrochloric acid were allowed to react at steam bath temperature for 7 hr, following the method of Ward (90), a sticky mass of material appeared and settled to the bottom of the flask. The supernatant aqueous layer was decanted, and the sticky mass was dissolved in 40 ml of hot absolute ethanol. Upon cooling more than 3 gm of shiny crystalline plates of benzhydryl ether (mp 109 - 110°; lit (61) mp 111°) was collected and dried. Nmr δ 7.30 (s, 20) and 5.40 (s, 2); ir 1600 (m), 1490 (m), 1450 (s), 1163 (m), 1082 (vs), 1050 (vs), 1022 (vs), and 913 cm^{-1} (m).

Benzhydryl diphenylacetate

From 200 ml of a benzene solution of 11.7 gm (55 mmole) of diphenylacetic acid (Distillation Products Industries) and 9.2 gm (50 mmole) of benzhydrol (Matheson Coleman and Bell) was removed approximately 1 ml of water as an azeotrope in 12 hr. The reaction mixture was extracted with 3x50 ml of saturated sodium bicarbonate; from these washings 2.1 gm of diphenylacetic acid was recovered upon acidification with hydrochloric acid. After extracting with 3x50 ml of distilled water the benzene layer was dried over magnesium sulfate for 2 hr. The benzene was removed under aspirator vacuum by a rotary evaporator, leaving behind benzhydryl diphenylacetate (mp 105 - 107°; lit (55) mp 106°) which was readily recrystallized from hexane to yield 16.9 gm (90%) of product. Nmr δ 7.20 (d, 20), 6.91 (s, 1), and 5.12 (s, 1); ir 1733 (vs), 1600 (m), 1493 (m), 1450 (m), 1257 (m), 1137 (vs), 1022 (m), 1000 (m), and 978 cm^{-1} (m).

Diphenylacetyl chloride

Following the procedure of Staudinger (83), a mixture of 10.6 gm (0.05 mole) of diphenylacetic acid (Distillation Products Industries) and 12 gm (0.1 mole) of thionyl chloride (Matheson Coleman and Bell) was heated on a steam bath until all the solid went into solution. The excess thionyl chloride was removed under water aspirator pressure in a rotary evaporator. The solid residue was recrystallized four times from hexane to yield 9 gm (78.5%) of diphenylacetyl chloride (mp 52.5 - 54.5°; lit (20) mp 56 - 57°). Nmr δ 7.25 (s, 10) and 5.39 (s, 1); ir 1810 (vs), 1780 (s), 1735 (m), 1605 (m), 1500 (s), 1455 (s), 1150 (m), 1080 (m), 1027 (m), 1007 (s), 983 (vs), and 913 cm^{-1} (m).

t-Butylperoxy diphenylacetate

Following the procedure of Bartlett and Gortler (9), the t-butyl hydroperoxide received from K and K Laboratories, Inc. as a 70% aqueous solution was purified by extracting approximately 15 ml of t-butyl hydroperoxide in 100 ml of redistilled petroleum ether with 3x50 ml of saturated sodium chloride. After drying over magnesium sulfate for 2 hr most of the petroleum ether was removed under aspirator vacuum on a rotary evaporator, the temperature of the pot remaining well below room temperature. The residue was distilled at 9-10 mm pressure; the pot temperature was kept below 38°. That fraction (about 10 ml) boiling at 27 - 28° was collected for use.

Then a solution of 2.60 gm (12.6 mmole) of diphenylacetyl chloride in 15 ml of ether was added dropwise to a stirred solution of 1.42 gm (18 mmole) of pyridine and 1.63 gm (18 mmole) of t-butyl hydroperoxide in 15 ml of pentane and 10 ml of ether kept at -5 - 0°. The straw-colored mixture was poured on crushed ice, and 30 ml of ether was added to dissolve the perester. Extraction with 3x50 ml of cold 10% sulfuric acid, with 3x50 ml of cold 10% sodium carbonate, and with 3x50 ml of cold distilled water was followed by drying the ether-pentane layer over magnesium sulfate for 1.5 hr. The organic layer was decanted, and most of the pentane and ether was stripped off under water aspirator pressure on a rotary evaporator at a temperature well below room temperature. The 20-30 ml of solution remaining was introduced onto a column of 9 gm of 60/100 mesh Florisil (E. H. Sargent and Co.) to remove any traces of t-butyl hydroperoxide. Approximately 75 ml of redistilled petroleum ether removed all of the perester from the column. The solvent was removed by rotary evaporation at reduced pressure at less than room temperature. The crystalline residue was taken up in hexane and recrystallized to yield a first crop of 1.49 gm (46.5%) of t-butylperoxy diphenylacetate (mp 58 - 60°; lit (9) mp 58.2 - 60.0°). A second crop of crystals was not isolated or used.

4,4'-Dichlorobenzhydryl oxalate

The water contained in 0.54 gm (4.2 mmole) of oxalic acid dihydrate (Baker Chemical Co.) was azeotroped off into a Dean-Stark trap with 25 ml of benzene in 5 hr. To the benzene-- oxalic acid mixture were added 1.92 gm (7.6 mmole) of 4,4'-dichlorobenzhydrol (Aldrich Chemical Co.) and 10 mg of p-toluenesulfonic acid.[1] After refluxing the mixture for 12 hr to remove the water produced in the reaction as an azeotrope, the reaction mixture was washed with equal volumes of saturated sodium bicarbonate twice and water twice, and the organic layer was dried over magnesium sulfate for 1 hr. The benzene was stripped off at reduced

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[1] Using concentrated sulfuric acid as catalyst instead of p-toluenesulfonic acid led only to a thick, intractable liquid as product; no oxalate was found.

pressure by rotary evaporator. The crystalline residue was taken up in and recrystallized from hexane to yield 1.60 gm (75.5%) of 4,4'-dichlorobenzhydryl oxalate (mp 142.5 - 143°). Nmr δ 7.32 (s, 16) and 6.90 (s, 2); in 1773 (s), 1750 (vs), 1600 (m), 1496 (vs), 1360 (m), 1290 (m), 1160 (vs), 1090 (vs), 1016 (vs), and 952 cm^{-1} (m); MW (mass spectrum) 560-562 m/e.

Anal. Calcd for $C_{28}H_{18}Cl_4O_4$: C, 60.03; H, 3.24; Cl, 25.30. Found: C, 60.07; H, 3.48; Cl, 25.40.

Benzyl oxalyl chloride

In a 1-l 2-neck flask fitted with a condenser were placed 44.8 gm (0.353 mole) of oxalyl chloride (Columbia Organic Chemicals Co., Inc.) and 2 volumes of carbon tetrachloride; to this solution stirred at 0° with a magnetic stirrer was added 34.1 gm (0.315 mole) of benzhydrol (Distillation Products Industries) in 100 ml of carbon tetrachloride over a period of 2.5 hr.[1] The mixture was then stirred for 1 hr at 0°, for 1.5 hr at room temperature, and for 7 hr at 40°. After this time no more hydrogen chloride was being evolved. Carbon tetrachloride was stripped off by a rotary evaporator, and the residue was distilled through a short Vigreux column to yield 46.24 gm (74%) of benzyl oxalyl chloride (bp 68 - 71° at 0.08-0.12 mm). Nmr δ 7.34 (s, 5) and 5.28 (s, 2); ir (in carbon tetrachloride) 1792 (vs), 1770 (vs), 1500 (w), 1455 (w), 1373 (w), 1257 (vs), 1233 (s), 990 (s), and 962 cm^{-1} (s).

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[1] T. H. Kinstle and R. L. Muntz, Ames, Iowa. Private communication. 1967.

Benzyl benzhydryl oxalate

A solution of 3.29 gm (17.9 mmole) of benzhydrol (Matheson Coleman and Bell) and 2.10 gm (20.8 mmole) of anhydrous triethylamine in 50 ml of anhydrous ether was cooled in an ice bath; then 3.55 gm (17.9 mmole) of benzyl oxalyl chloride was added dropwise. In 10-15 min the reaction mixture was filtered to remove the triethylammonium chloride; the salt was washed with ether. The combined filtrates were washed with 2 volumes of distilled water and dried over magnesium sulfate. The ether was removed under aspirator pressure, and the residual oil was crystallized from hexane to yield 5.23 gm (84%) of benzyl benzhydryl oxalate (mp 51 - 53°; mp[1] 49 - 50°). Nmr δ 7.32 (s, 15), 6.98 (s, 1), and 5.24 (s, 2); ir 1772 (s), 1747 (vs), 1494 (w), 1455 (w), 1300 (m), 1156 (vs), 1075 (m), 940 (m), and 905 cm^{-1} (w).

Potassium methyl oxalate

Following the published procedure (22, 36), a hot solution of 59 gm (0.50 mole) of methyl oxalate (Distillation Products Industries) in 59 gm of methanol was prepared, and to this solution 49 gm (0.50 mole) of anhydrous potassium acetate (Matheson Coleman and Bell) in 49 gm of warm distilled water was added dropwise. The reaction was refluxed until the disappearance of potassium acetate was observed. The reaction mixture was refrigerated overnight and was then concentrated to one-half volume by a rotary evaporator. Treatment of this viscous liquid with 1 volume

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[1] T. H. Kinstle and R. L. Muntz, Ames, Iowa. Private communication. 1967.

of absolute ethanol and 2 volumes of ether produced a crystalline compound which was filtered and vacuum dried to yield 64.7 gm (91%) of potassium methyl oxalate (mp 195 - 196°; lit (36) mp 197°).

Methyl oxalyl chloride

Following the published procedure (36), treatment of 28.4 gm (0.2 mole) of potassium methyl oxalate with 16 ml of thionyl chloride (Matheson Coleman and Bell) added dropwise led to, after heating the reaction for 3 hr on a steam bath, a distilled yield of 21.55 gm (88%) of methyl oxalyl chloride (bp 114 - 116° at 1 atm; lit (36) bp 117 - 118°). Ir (in carbon tetrachloride) 1797 (s), 1770 (vs), 1434 (w), 1260 (s), 1018 (s), and 893 cm^{-1} (m).

Methyl benzhydryl oxalate

Dropwise addition of 2.00 gm (16.3 mmole) of methyl oxalyl chloride to a solution of 3.00 gm (16.3 mmole) of benzhydrol and 1.70 gm (16.8 mmole) of dry triethylamine in 30 ml of anhydrous ether produced triethylammonium chloride which was filtered and washed with ether. Ether was removed from the filtrate by a rotary evaporator leaving a white solid which was recrystallized from hexane--dichloromethane to yield 3.72 gm (84%) of methyl benzhydryl oxalate (mp 64 - 66°). Nmr δ 7.32 (m, 10), 6.97 (s, 1), and 3.77 (s, 3); ir 1766 (vs), 1740 (vs), 1447 (w), 1312 (m), 1300 (m), 1150 (vs), 978 (w), 946 (m), and 902 cm^{-1} (w); MW (mass spectrum) 270 m/e.

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.33; H, 5.25.

Methyl benzhydryl ether

As in the method of Kostanecki and Lampe (56), a solution of 10 gm (54.4 mmole) of benzhydrol (Matheson Coleman and Bell) and 1 ml of concentrated hydrochloric acid in 80 ml of absolute methanol was refluxed for 24 hr on a steam bath. The excess methanol was stripped off in a rotary evaporator. The residue was taken up in 75 ml of dichloromethane and was extracted with 2x75 ml of saturated sodium bicarbonate. The organic layer was dried over magnesium sulfate and filtered, and the solvent was removed under aspirator pressure. The residue was distilled under vacuum, and 9.35 gm (87%) of methyl benzhydryl ether (bp 87 - 89^{o} at 0.35 mm; lit (46) bp 129^{o} at 5 mm) was isolated. Nmr δ 7.30 (m, 10), 5.20 (s, 1), and 3.32 (s, 3); ir 2820 (w), 1600 (w), 1490 (m), 1450 (m), 1350 (w), 1127 (s), 1087 (vs), 1073 (vs), 1026 (w), 965 (m), and 910 cm^{-1} (w).

Methyl diphenylacetate

After the manner of Rattner (77), absolute methanol containing 10 gm (47.2 mmole) of diphenylacetic acid (Distillation Products Industries) and 1 ml of concentrated hydrochloric acid was refluxed for 12 hr. The excess methanol was removed by rotary evaporation, and the crude product was dissolved in 75 ml of dichloromethane. After washing the dichloromethane solution with 2x50 ml of saturated sodium bicarbonate and drying over magnesium sulfate, the solvent was stripped off under aspirator pressure. Recrystallization of the residue from hexane yielded 9.78 gm (92%) of methyl diphenylacetate (mp 58.5 - 59.5^{o}; lit (77) mp 59 - 60^{o}).

Nmr δ 7.26 (s, 10), 5.02 (s, 1), and 3.65 (s, 3); ir 1730 (vs), 1600 (w), 1495 (m), 1450 (m), 1430 (m), 1345 (m), 1300 (m), 1270 (m), 1150 (s), 1075 (w), and 1007 cm^{-1} (m).

Methyl carbazate

According to the method of Diels (35), after dropwise addition of 50 gm (1 mole) of hydrazine hydrate (Matheson Coleman and Bell) to 90 gm (1 mole) of methyl carbonate (Aldrich Chemical Company) in a 500-ml round-bottom flask cooled in ice was completed, the reaction mixture was allowed to stand at room temperature for 3 hr; the water and methanol produced were then removed under aspirator vacuum by rotary evaporation. The solid residue was recrystallized from hexane--dichloromethane to yield 80.5 gm (89.5%) of methyl carbazate (mp 67 - 69°; lit (35) mp 73°). Nmr δ 6.9 (vbs, ~1), 3.90 (bs, ~2) and 3.70 (s, 3); ir 3425 (m), 1720 (vs), 1628 (m), 1479 (s), 1355 (w), 1265 (s), and 1057 cm^{-1} (m).

Methyl 3-tritylcarbazate

Using a variation of the method of Carpino, Terry, and Crowley (24), 11.43 gm (41.1 mmole) of trityl chloride (Fisher Scientific Company) in 20 ml of benzene was added dropwise to 3.7 gm (41.1 mmole) of methyl carbazate in 25 ml of pyridine. After standing 1 hr at room temperature the pyridinium chloride formed was removed by extracting the reaction mixture with an equal volume of water. Dichloromethane was added to the organic layer to increase the solubility of methyl 3-tritylcarbazate. The organic layer was dried over anhydrous magnesium sulfate and filtered; most of the pyridine, benzene, and dichloromethane were removed in a rotary evaporator. The residue was recrystallized from hexane--dichloromethane twice to yield 10.79 gm (79%) of methyl 3-tritylcarbazate (mp 175 - 177°). Nmr δ 7.6-7.9 (m, 15), 5.56 (s, 1), 4.47 (bs, 1), and 3.50 (s, 3); ir 3335 (w), 2990 (bw), 1725 (bs), 1590 (w), 1487 (s), 1442 (s), 1355 (m), 1243 (m), 1157 (s), and 905 cm^{-1} (m).

Anal. Calcd for $C_{21}H_{20}N_2O_2$: C, 75.91; H, 6.02; N, 8.43. Found: C, 76.11; H, 6.12; N, 8.39.

Methyl tritylazocarboxylate

After the manner of Carpino, Terry, and Crowley (24), 8.37 gm (25.2 mmole) of methyl 3-tritylcarbazate and 2.00 gm (25.2 mmole) of pyridine in 50 ml of dichloromethane were cooled to 0°; to this magnetically stirred solution was added 4.50 gm (25.2 mmole) of N-bromosuccinimide (Distillation Products Industries) which had been recrystallized from water. As the crystalline N-bromosuccinimide was added, the reaction mixture became yellow in color. Upon completion of the addition of N-bromosuccinimide, the reaction was stirred at room temperature for 10 min. The reaction mixture was then washed with 50 ml of water and 2x50 ml of 10% potassium carbonate and dried over magnesium sulfate. The yellow solid left upon removal of the solvent under aspirator pressure was recrystallized from pentane--dichloromethane to yield 7.56 gm (91%) of methyl tritylazocarboxylate (mp 98 - 100° with decomposition) in what appeared to be two crystalline forms--yellow crystals and orange crystals which are converted to the yellow crystals with explosive violence at ~90°. Both kinds of crystals were examined by nmr; no solvent of crystallization was found. Nmr δ 7.20 (m, 15) and 3.86 (s, 3); ir 1765 (vs), 1595 (w), 1489 (w), 1440 (m), 1250 (bs), 1026 (w), 1003 (w), 949 (w), 898 (w), and 885 cm^{-1} (w).

Phenyl carbazate

To 89.4 gm (0.418 mole) of phenyl carbonate (Matheson Coleman and Bell) dissolved in 300 ml of dichloromethane was added 21.13 gm (0.422 mole) of hydrazine hydrate (Matheson Coleman and Bell); the reaction was allowed to stand overnight at room temperature. The water formed during the reaction was drawn off, and the organic layer was dried over magnesium sulfate. After filtration to remove the magnesium sulfate the solution was concentrated to about half of the original volume by rotary evaporation under vacuum. Anhydrous ether was added until all of the phenyl carbazate was precipitated. The phenol by-product remained soluble in the ether--dichloromethane. The product was collected by filtration and was recrystallized from hexane--dichloromethane yielding 36.5 gm (58%) of phenyl carbazate (mp 103 - 104°; lit (68) mp 105°). Nmr δ 7.23 (m, 5), 6.65 (vbs, 1), and 3.86 (bs, 2); ir 3430 (w), 1736 (vs), 1628 (m), 1593 (w), 1465 (vs), 1350 (w), 1250 (m), 1163 (m), 1067 (w), 1026 (m), 1005 (w), and 910 cm^{-1} (w).

Phenyl 3-tritylcarbazate

Analogously to the preparation of methyl 3-tritylcarbazate, a solution of 56.8 gm (0.199 mole) of trityl chloride in 100 ml of benzene was added dropwise to 30.3 gm (0.199 mole) of phenyl carbazate in 125 ml of pyridine. After several hours at room temperature the reaction mixture was diluted with dichloromethane and extracted with an equal volume of water to remove the pyridinium chloride. The organic layer was dried over magnesium sulfate, filtered, and evaporated to dryness under aspirator pressure. The residue was recrystallized from hexane--dichloromethane to give 61.0 gm (78%) of phenyl 3-tritylcarbazate (mp 161 - 162°). Nmr δ 7.30 (m, 20), 5.92 (s, 1), and 4.53 (bs, 1); ir 3330 (m), 2970 (bw), 1750 (bvs), 1595 (m), 1487 (vs), 1444 (s), 1423 (s), 1352 (m), 1152 (s), 1130 (s), 1100 (m), 1025 (m), 1000 (m), 940 (m), and 905 cm^{-1} (m).

Anal. Calcd for $C_{26}H_{22}N_2O_2$: C, 79.16; H, 5.62; N, 7.10. Found: C, 79.32; H, 5.92; N, 6.95.

Phenyl tritylazocarboxylate

Oxidation of 6.65 gm (16.9 mmole) of phenyl 3-tritylcarbazate in the presence of 1.33 gm (16.9 mmole) of pyridine dissolved in 50 ml of dichloromethane was carried out at 0° by addition of 3.00 gm (16.9 mmole) of crystalline N-bromosuccinimide over a period of 5 min. A light yellow color appeared and persisted as the N-bromosuccinimide was added. Upon completion of the addition of N-bromosuccinimide the reaction was stirred at room temperature for 10 min. The workup procedure entailed washing the reaction mixture with 50 ml of water and with 2x50 ml of 10% potassium carbonate and drying over magnesium sulfate. The solvent was removed in a rotary evaporator, and the yellow solid residue was recrystallized from pentane--dichloromethane to produce 4.67 gm (71%) of phenyl tritylazocarboxylate (mp 105 - 106° with decomposition). Nmr δ 7.26 (m); ir 1778 (vs), 1590 (m), 1490 (s), 1446 (m), 1170 (m), 1156 (m), 1080 (w), 1067 (w), 1025 (w), and 1005 cm^{-1} (w).

Triphenylacetyl chloride

In a manner similar to that of Jones and Hurd (52), an excess (30 ml) of newly opened thionyl chloride (Mathescn Coleman and Bell) was refluxed with 8.34 gm (29 mmole) of triphenylacetic acid (Aldrich Chemical Co.) on a steam bath for ~45 min. The excess thionyl chloride was removed under aspirator pressure in a rotary evaporator, and the crystalline residue was recrystallized from hexane to yield 8.13 gm (92%) of triphenylacetyl chloride (and an unknown compound) (mp 122 - 125°; lit (41a, 25a) mp 128°). Ir (in carbon tetrachloride) 3030 (m), 1950 (w), 1810 (vs), 1780 (vs), 1600 (w), 1495 (s), 1450 (s), 1325 (w), 1185 (w), 1086 (m), 1036 (vs), 1015 (s), 996 (s), 938 (m), 914 (w), and 898 cm^{-1} (w).

Benzyl triphenylacetate

Following the method of Norris and Cresswell (73), a solution of 2.73 gm (8.88 mmole) of triphenylacetyl chloride in 10 ml of benzyl alcohol (Distillation Products Industries) was refluxed at 225° for 18 hr. A small amount of water was formed during the reaction. The excess benzyl alcohol (bp 75 - 80° at 4-5 mm) was removed by distillation through a short Vigreux column. From recrystallization in hexane was obtained 1.72 gm (51%) of benzyl triphenylacetate (mp 98 - 99°; lit (73) mp 99 - 99.5°). Nmr δ 7.17 (s, 20) and 5.21 (s, 2); ir 1950 (w), 1875 (w), 1810 (w), 1725 (vs), 1600 (m), 1487 (s), 1445 (s), 1365 (w), 1170 (s), 1077 (m), 1005 (s), 973 (s), and 905 cm^{-1} (w).

Benzyl trityl ether

According to the procedure of Pratt and Draper (75), in a 250-ml round-bottom flask fitted with a Dean-Stark trap and a condenser 8.50

gm (3.26 mmole) of tritanol (Matheson Coleman and Bell), 3.52 gm (3.26 mmole) of benzyl alcohol, and ~50 mg of p-toluenesulfonic acid dissolved in 115 ml of benzene were heated at reflux for 5 hr; ~0.5 ml of water was collected in the trap. The reaction product was washed with 2x75 ml of saturated sodium bicarbonate and 2x75 ml of distilled water. The benzene was removed with a rotary evaporator after the organic layer was dried over magnesium sulfate. Recrystallization from absolute ethanol led to 9.0 gm (79%) of benzyl trityl ether (mp 101 - 103°; lit (75) mp 105.5 - 106°). Nmr δ 7.35 (m, 20), and 4.26 (s, 2); ir 2850 (w), 1950 (w), 1870 (w), 1820 (w), 1600 (m), 1490 (s), 1445 (vs), 1375 (s), 1310 (m), 1150 (s), 1085 (vs), 1053 (vs), 1000 (s), 982 (s), 945 (m), and 900 cm^{-1} (s).

Potassium phenylacetate

Following the method of Davies and Thomas (30), this salt was prepared by neutralizing 4.50 gm (33.1 mmole) of phenylacetic acid dissolved in distilled water with an aqueous solution containing 4.57 gm (33.1 mmole) of potassium carbonate. The water was evaporated, and 5.63 gm (98%) of potassium phenylacetate was recrystallized from acetone--ethanol and dried in a vacuum desiccator.

Trityl bromide

Following the published method (49) steam bath heat was applied to a 500-ml round-bottom flask fitted with a condenser and stirrer which contained 95 gm (0.37 mole) of tritanol (Distillation Products Industries) in 35 ml of benzene. When refluxing from the addition of 14 ml of acetyl bromide (Matheson Coleman and Bell) subsided, an additional 27 ml of acetyl bromide was added, 3 ml at a time. Upon completion of the addition, the reaction was stirred under reflux for 30 min. After cooling to room temperature 80 ml of redistilled petroleum ether (bp 25 - 35°) was added, and the reaction mixture was cooled in an ice bath for 2 hr. The product was rapidly filtered, washed with 60 ml of redistilled petroleum ether, and transferred to a vacuum desiccator, where it was stored until use.

From the reaction 113 gm (96%) of light yellow crystals of trityl bromide (mp 152°; lit (81) mp 152°) was isolated. Ir 1955 (w), 1890 (w), 1813 (w), 1600 (m), 1485 (vs), 1442 (vs), 1315 (s), 1142 (m), 1112 (w), 1078 (m), 1030 (w), 1000 (s), and 890 cm^{-1} (s).

Trityl phenylacetate

In a manner quite similar to that of Berlin and coworkers (16), 5.60 gm (17.3 mmole) of trityl bromide, 3.63 gm (20.8 mmole) of potassium phenylacetate, and 50 ml of benzene in a 250-ml 3-neck round-bottom flask were refluxed for 4 hr with rapid stirring (Lightnin' stirrer). The mixture was filtered while warm and washed with benzene. Benzene was removed by rotary evaporator under aspirator pressure. The solid residue upon recrystallization twice from hexane produced 0.52 gm (12%) of tritanol (identified by mp and ir) and 4.54 gm (70%) of trityl phenylacetate (mp 69 - 71°). Nmr δ 7.17 (m, 20) and 3.60 (s, 2); ir 1737 (vs), 1600 (w), 1490 (m), 1450 (m), 1130 (s), 983 (s), 960 (m), and 900 cm^{-1} (m).

Anal. Calcd for $C_{27}H_{22}O_2$: C, 85.69; H, 5.86. Found: C, 86.62, 85.05, 84.02; H, 6.05, 5.97, 6.09.

This compound is apparently moisture sensitive in view of the inconsistent analyses (same material was submitted ~2 weeks after the first sample; then, this material was recrystallized 4 times from hexane and submitted in a vial sealed under vacuum) and nmr analysis which after ~2 weeks showed a new, appreciable peak at 3.50 δ and should be stored under vacuum. The pyrolysis data obtained should be valid since all the samples pyrolyzed were degassed and sealed under vacuum within 3 days of the above preparation.

Methyl triphenylacetate

Following the procedure of Norris and Cresswell (73), a solution of 2.72 gm (8.88 mmole) of triphenylacetyl chloride (?), 40 ml of anhydrous methanol, and 45 ml of benzene was refluxed for 18 hr. The solvents were removed by rotary evaporation, and the crystalline residue was recrystallized from hexane to produce 1.96 gm (73%) of methyl triphenylacetate (mp 182 - 184°; lit (42) mp 182°). Nmr δ 7.11 (d, 15) and 3.67 (s, 3); ir 1955 (w), 1875 (w), 1815 (w), 1725 (vs), 1595 (m), 1486 (s) 1445 (s), 1430 (s), 1162 (m), 1077 (w), 1010 (vs), and 885 cm^{-1} (m).

Phenyl triphenylacetate

Following the method of Schmidlin and Hodgson (80a), a solution of 2.68 gm (8.73 mmole) of triphenylacetyl chloride (?) in 10.13 gm of phenol (Mallinckrodt Chemical Works) was refluxed for 18 hr. The reaction mixture was taken up in 25 ml of dichloromethane and was washed with 4x20 ml of 10% sodium hydroxide and with 2x20 ml of distilled water. The organic layer was dried over magnesium sulfate before the dichloromethane was removed by rotary evaporation. Recrystallization from hexane led to isolation of 2.45 gm (77%) of phenyl triphenylacetate (mp 124 - 126°; lit (80a) mp 123 - 124°). Ir 1955 (w), 1880 (w), 1815 (w), 1755 (vs), 1595 (s), 1490 (s), 1447 (m), 1156 (vs), 1080 (w), 1020 (w), 1000 (w), 970 (s), 932 (w), and 900 cm^{-1} (w).

Pyrolyses

Description of high temperature baths and pyrolysis apparatus

A maximum temperature of ~275° can be attained with a bath containing Dow Corning 550 silicone fluid. Heat was supplied with a coil of Chromel wire connected to a Variac. A thermometer was used to read the temperature. One or two samples could be accommodated.

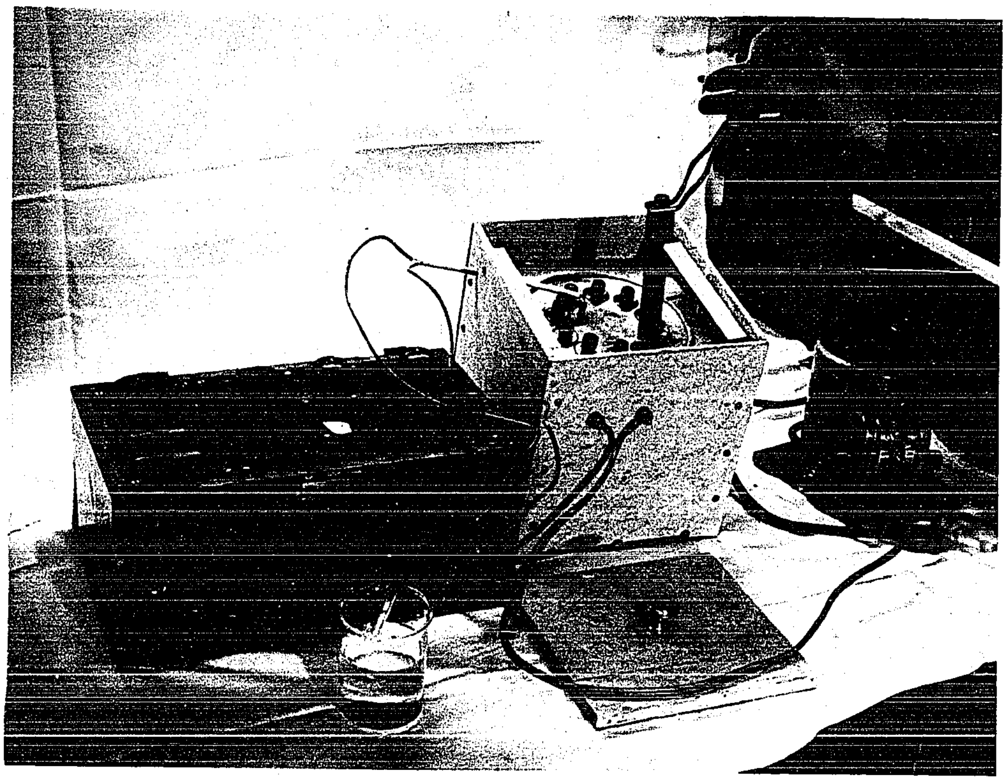
A piece of 0.25" steel tubing 3.5" in diameter and 9.5" tall was welded shut on one end with a plate of 0.25" steel. The tubing was wrapped with asbestos ribbon, Chromel heating wire, and again with asbestos ribbon. A wire cage containing one, two, or three samples could be suspended in this air bath, and the open top was then covered with pieces of asbestos to minimize air circulation. Fair temperature control up to a maximum of 375° was realizable; a thermometer was used as the temperature sensing device.

Also used in some experiments for temperatures up to 350° was a Woods metal bath heated by a Tirrill burner. One or two samples at a time could be pyrolyzed in this way.

For extremely good constant temperature control such as is required for kinetic studies, the apparatus in the following description and in Figure 1 was made. A round block of aluminum 6" in diameter and 6" long was wrapped with asbestos, wound with enough no. 20 Chromel heating wire to attain a maximum temperature of 500°, and again wrapped with asbestos.

Evenly spaced holes for 10 samples, each 0.875" in diameter, each 4.5" from the axis of the cylinder, and each 5" deep, were drilled into the block. One hole 0.25" in diameter and 3" deep for the thermocouple was drilled between two of the sample holes. Each of the 10 sample holes was expanded to 1" in diameter and to a depth of 1". Ten stainless steel plugs, each 1" in diameter and 1" deep, were ground to fit loosely in the sample holes and sit on the ledge of the inner hole. Each plug had a hook on the bottom side for attaching sample holders and a "knob" on the top for pulling out the plug (and sample). Ten sample holders were made of stainless steel tubing 22 mm in diameter and were fitted

Figure 1. Aluminum block constant temperature bath



with wire bails.

The aluminum block was placed in a box made of Transite insulation board; the box was filled with blown mica and covered with a Transite lid. A Variac supplied the energy to heat the bath, and a thermocouple attached to a Leeds and Northrup potentiometer measured the temperature of the bath.

The apparatus for pyrolysis in the gas phase[1] consisted of a 0.75" x 12" vycor tube mounted horizontally, packed with pieces of vycor tubing, and encased in a 12" electric furnace. At one end of the tube was attached by a standard taper ground glass joint a 0.75" x 1.75" tube closed at one end. This tube which held the starting material was encased in a slightly larger test tube wrapped with heating tape. On the other end of the pyrolysis tube was attached by means of a ball and socket joint a u-shaped trap made from 15" of 0.5" pyrex tubing with indentations. The trap was directly connected to a vacuum system. Temperature of the pyrolysis tube was controlled by a Variac and monitored by use of a thermocouple and a Leeds and Northrup potentiometer.

Thermal stabilities of some solvents

A series of 5 solvents was degassed 3 times and sealed under vacuum in one-half of 15x125 mm test tubes. These solvents--biphenyl, phenyl ether, 1,3,5-triisopropylbenzene, naphthalene, and 1-chloronaphthalene--were removed after 6.5 hr, 15.5 hr, and 48.5 hr at 350^{o} and visually examined. Only 1-chloronaphthalene and naphthalene experienced some

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[1] W. S. Trahanovsky, C. C. Ong, and J. A. Lawson, Ames, Iowa. Private communication. 1968.

slight yellowing during this period.

The solvent tubes were then left in the aluminum block bath at 350° for 30 days, after which time they were cooled, opened, and examined by glpc. Comparison of the pyrolyzed samples with unpyrolyzed samples showed that biphenyl, phenyl ether, and naphthalene experienced no detectable decomposition while 1-chloronaphthalene which became black and gave off a noxious odor upon opening and 1,3,5-triisopropylbenzene experienced measurable decomposition. No accurate estimate for the amounts of decomposition of the latter two solvents was made in this qualitative experiment.

Thermal conductivity ratios of thermal decomposition products

Reference solutions containing known amounts of the identified thermal decomposition products and using known amounts of benzil (or diphenylmethane) as internal standard were prepared and analyzed by glpc as in Tables 16 and 17.

Separation and identification of the products from neat pyrolysis of benzhydryl oxalate

A sample of benzhydryl oxalate weighing 2.00 gm (4.74 mmole) was flushed with nitrogen for at least 15 min and was then pyrolyzed at 275° for 30-35 min in a 50 ml flask fitted with an air reflux condenser. During pyrolysis 0.316 gm (7.18 mmole) of carbon dioxide was lost. The light yellow pyrolysate was separated by adsorption chromatography[1] on

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[1] Alumina is a poor choice for a column material, for it completely hydrolyzes benzhydryl oxalate and benzhydryl diphenylacetate.

Table 16. Analysis of reference solutions of thermal decomposition products using benzil as internal standard

Compound R	$\left(\frac{\text{Mmole benzil}}{\text{Mmole R}}\right)_{\text{ref}}$	$\left(\frac{\text{Area benzil}}{\text{Area R}}\right)_{\text{ref}}^{a}$
Toluene	1.31	2.09
Phenol	0.376	0.738
Benzaldehyde	0.485	0.836
Diphenylmethane	0.968	1.07
Benzophenone	1.16	1.23
Triphenylmethane	1.14	1.00
1,1,2-Triphenylethane	1.21	1.04
Benzyl diphenylacetate	1.48	1.36
1,1,2,2-Tetraphenylethane	1.72	1.37
Methyl triphenylacetate	1.11	0.850
Methyl 4-benzhydrylbenzoate	0.976	0.741
Methyl 4-carbomethoxyphenyl-diphenylacetate	1.25	0.877

[a] Average value of 2 injections.

Table 17. Analysis of reference solution of pyrolysate products using diphenylmethane as internal standard

Compound R	$\left(\frac{\text{Mmole DPM}^{a}}{\text{Mmole R}}\right)_{\text{ref}}$	$\left(\frac{\text{Area DPM}^{a}}{\text{Area R}}\right)_{\text{ref}}$
Benzaldehyde[b]	0.587	0.926
Triphenylmethane[b]	1.65	1.21

[a] Diphenylmethane.

[b] Average of 2 injections.

a 60/100 mesh Florisil (E. H. Sargent and Co.) column into the following components.

1,1,2,2-Tetraphenylethane was desorbed by pentane and was recrystallized from carbon tetrachloride to yield 0.82 gm (2.46 mmole) of white crystals (mp 209.5 - 210° lit (19) mp 209 - 210°). Nmr δ 7.11 (d, 20) and 4.78 (s, 2); ir 1940 (w), 1870 (w), 1800 (w), 1600 (s), 1495 (s), 1450 (s), and 1070 cm^{-1} (s).

Benzhydryl diphenylacetate was eluted with 75% pentane--25% benzene. Recrystallization from hexane gave 0.38 gm (1.00 mmole) of white solid (mp 106-108°; lit (55) mp 106°). Nmr δ 7.20 (d, 20), 6.93 (s, 1), and 5.13 (s, 1); ir 1735 (vs), 1600 (m), 1495 (m), 1450 (m), 1258 (m), 1140 (vs), 1020 (m), 1000 (m), and 978 cm^{-1} (m).

Benzhydrol was eluted with 25% pentane--75% benzene. Recrystallization from hexane led to the isolation of 0.12 gm (0.65 mmole) of crystals (mp 64 - 66°; lit (60) mp 67 - 68°) having nmr and ir spectra identical to those of authentic benzhydrol (Matheson Coleman and Bell). Nmr δ 7.32 (s, 10), 5.78 (s, 1), and 2.34 (bs, 1); ir 3570-3450 (bm), 1595 (m), 1490 (s), 1450 (vs), 1010 (vs), and 910 cm^{-1} (m).

No nmr peaks for benzhydrol were ever observed in the pyrolysates of benzhydryl oxalate. Upon passing benzhydryl oxalate through a Florisil column some benzhydrol (mp 64°) was collected, but no benzhydrol was collected upon passing benzhydryl diphenylacetate through a Florisil column.

Analysis of the pyrolysates from benzhydryl oxalate by nmr

Samples of benzhydryl oxalate were pyrolyzed in an oil bath either neat or in purified[1] phenyl ether under the conditions in Table 18. Following pyrolysis diphenylmethane was added as an internal standard, and the integration areas of the characteristic nmr absorptions of 1,1,2,2-tetraphenylethane and benzhydryl diphenylacetate were measured as in Table 19.

Table 18. Pyrolysis conditions for samples of benzhydryl oxalate

Run	Amount of oxalate, mmole	Amount of phenyl ether, mmole	Temp, °C	Period of heating, hr
1	0.264	5.89	225	2
2	0.141	3.26	225	2
3	0.143	3.26	225	10
4	1.20	--[a]	200	2
5	0.198	--[a]	200	2.25
6	0.327	--[a]	225	1[b]
7	0.215	4.08	225	1[b]

[a] Pyrolysis of neat benzhydryl oxalate.

[b] Pyrolysis was carried out in the presence of oxygen.

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[1] Approximately 60 gm of phenyl ether (Matheson Coleman and Bell) was extracted with 3x100 ml of 10% sodium hydroxide and with 3x100 ml of distilled water and were dried over magnesium sulfate. The phenyl ether was then distilled through a vacuum-jacketed Vigreux column; only the fraction boiling at 58° under 0.18 mm pressure was collected for use.

Table 19. Analyses of benzhydryl oxalate pyrolysates[a]

Run	Amount of DPM,[b] mmole	Integration area DPM[b,c]	TPE[d,e]	BHDPA[f,g]
1	0.210	150	81	18
2	0.128	103	46	11
3	0.133	114	76	20
4	0.123	39	63	60
5	0.122	198	70	52
6[h,i]	0.117	68	10	12
7[j]	0.117	39	0	0

[a] No nmr peaks for benzhydrol were observed.

[b] DPM--diphenylmethane.

[c] Peak at 3.94δ (2 H) was integrated.

[d] TPE--1,1,2,2-tetraphenylethane.

[e] Peak at 4.77δ (2 H) was integrated.

[f] BHDPA--benzyl diphenylacetate.

[g] Peak at 5.10δ (1 H) was integrated.

[h] Integration area of benzhydryl ether--10.

[i] Benzophenone is the major product (estimated to be 0.145 mmole).

[j] Presumably benzophenone is the major product, but it could not be quantitatively determined by nmr because of the solvent, phenyl ether.

Stability of benzhydryl diphenylacetate

Benzhydryl diphenylacetate was heated under nitrogen at 226° for 1.25 hr. Based on nmr analysis, < 3% decomposition occurred.

Pyrolysis of 1,1,2,2-tetraphenylethane and benzhydryl diphenylacetate in phenyl ether

An equimolar amount of 1,1,2,2-tetraphenylethane and benzhydryl diphenylacetate in phenyl ether solution was heated under nitrogen at 225° for 24 hr. Nmr analysis showed that 75% of the ethane and ester was still present.

Pyrolysis of 1,1,2,2-tetraphenylethane and benzhydryl diphenylacetate in the presence of oxygen

Oxygen was passed through an approximately equimolar amount of 1,1,2,2-tetraphenylethane and benzhydryl diphenylacetate while it was heated at 225° for 1 hr. At least 90% of the ethane and ester was recovered unchanged as shown by nmr analysis using diphenylmethane as an internal standard.

Pyrolysis of an equimolar mixture of benzhydryl and benzhydryl-α-d_1 oxalate

A mixture of 0.128 gm (0.304 mmole) of benzhydryl oxalate and 0.127 gm (0.300 mmole) of benzhydryl-α-d_1 oxalate in 2.40 gm (1.41 mmole) of phenyl ether was heated in a nitrogen atmosphere at 225° for 23 hr. The cooled pyrolysate was dissolved in 5 ml of hexane. When the mixture was cooled to -80°, most of the pyrolysis products crystallized, and most of the phenyl ether remained in solution. The white solid was filtered and treated with hexane in a similar fashion five more times. The white solid was recrystallized from hexane, and the crystals which were tetraphenylethane were submitted to mass spectral analysis. Removal of the hexane and phenyl ether from the solution by distillation under vacuum yielded a solid residue. This residue was recrystallized from hexane. The crystals were largely tetraphenylethane and were separated from the mother liquor which contained the ester. Removal of the hexane gave a solid mass which was submitted to mass spectral analysis.

In Tables 20 and 21 are presented the pertinent mass spectral data and calculated isotope distributions for d_0, d_1, and d_2 species (peaks > (P+3) were negligible). The natural isotope distribution in the oxalate-d_2 was assumed to be the same as that of the oxalate-d_0.

Table 20. Mass spectral data for tetraphenylethane[a] isolated from the pyrolysates of natural benzhydryl oxalate and a mixture of natural and deuterated benzhydryl oxalates

m/e		Intensity of natural sample	Intensity of mixed sample	Calcd peaks for d_0	Calcd peaks for d_1	Calcd peaks for d_2
334	P	100	16.8	16.8	--	--
335	P+1	29.5	36.9	5.0	31.9	--
336	P+2	7.9	32.4	1.3	9.4	21.7
337	P+3	--[b]	13.8	--	2.5	6.4

[a] These values are averages of three runs at 17 eV with a mean deviation for each value of < 2%.

[b] Too small to measure accurately.

Table 21. Mass spectral data for benzhydryl diphenylacetate[a] isolated from the pyrolysates of natural benzhydryl oxalate and a mixture of natural and deuterated benzhydryl oxalates

m/e		Intensity of natural sample	Intensity of mixed sample	Calcd peaks for d_0	Calcd peaks for d_1	Calcd peaks for d_2
378	P	100	39.7	39.7	--	--
379	P+1	33.2	23.2	13.2	10.0	--
380	P+2	6.9	29.0	2.7	3.3	23.0
381	P+3	--[b]	8.2	--	0.7	7.6

[a] These values are averages of four runs for the natural sample and three runs for the deuterated at 70 eV with a mean deviation for each value of $< 2.5\%$.

[b] Too small to measure accurately.

Attempted induced decomposition of benzhydryl oxalate with benzhydryl radicals in benzene solution

Nitrogen was bubbled for 2 min through a solution of 0.084 gm (0.200 mmole) of benzhydryl oxalate and 0.057 gm (0.200 mmole) of *t*-butylperoxy diphenylacetate in 1.29 gm of benzene. After the solution was heated under nitrogen for 2.25 hr at 70°, most of the benzene was distilled at atmospheric pressure.

Analysis of the residue by nmr showed that decomposition of the peroxy ester was complete (no. 5.01 δ peak), no benzhydryl diphenylacetate had formed (no 5.12 δ peak), and a large amount of oxalate was untouched (peak at 6.95 δ). An ir spectrum of the residue showed the strong oxalate carbonyl doublet at 1770-1750 cm^{-1}.

Products identified in the residue from their characteristic nmr absorptions included benzhydryl t-butyl ether (5.55 δ), benzhydryl ether (5.42 δ), tetraphenylethane (4.75 δ), t-butanol (6.36 δ), and acetone (1.56 δ).

Neat pyrolysis of 4,4'-dichlorobenzhydryl oxalate

When 4,4'-dichlorobenzhydryl oxalate was recrystallized from carbon tetrachloride, two molecules of carbon tetrachloride per molecule of oxalate were incorporated into the crystalline structure as indicated by analysis. A sample of this carbon tetrachloride-solvated oxalate weighing 1.86 gm (2.14 mmole) was flushed with nitrogen and was then pyrolyzed at 275° for 30 min. During pyrolysis 0.68 gm (1.72 mmole) of carbon tetrachloride and carbon dioxide was lost.

Yellow-orange crystals formed during the pyrolysis and were filtered before the remainder of the red-brown pyrolysate was separated by adsorption chromatography on a 60/100 mesh Florisil (E.H. Sargent and Co.) column. The filtered crystals were recrystallized with difficulty from carbon tetrachloride and chlorobenzene to give 0.55 gm (1.17 mmole) of 4,4',4",4"'-tetrachloro-sym-tetraphenylethane (mp 358 - 360° with decomposition; lit (70) mp 350 - 360° with decomposition). The nmr spectrum of this compound was not obtainable, due to its sparing solubility in the common organic solvents. Ir (potassium bromide pellet) 1495 (vs), 1410 (m), 1087 (vs), 1012 (vs), 813 (s), 788 (vs), and 735 cm^{-1} (m); MW (mass spectrum) 470-474 m/e.

4,4'-Dichlorobenzhydryl 4,4'-dichlorodiphenylacetate was eluted from the Florisil column with 75% pentane--25% benzene. Upon recrystallization from hexane 0.30 gm (0.58 mmole) of fluffy, white crystals (mp 125 - 126°; lit (43) mp 118°) was obtained. Nmr δ 7.18 (m, 16), 6.82 (s, 1), and 5.04 (s, 1); ir 1740 (vs), 1600 (m), 1487 (s), 1400 (m), 1126 (vs), 1090 (vs), 1013 (s), and 983 cm^{-1} (s); MW (mass spectrum) 511-515 m/e.

Anal. Calcd for $C_{27}H_{18}Cl_4O_2$: C, 62.82; H, 3.51; Cl, 27.46. Found: C, 62.72; H, 3.58; Cl, 27.58.

4,4'-Dichlorobenzhydrol was eluted with 25% pentane--75% benzene. Recrystallization from hexane gave 0.10 gm (0.40 mmole) of white solid (mp 90 - 92°; lit (69) mp 94°) having nmr and ir spectra identical to those of authentic 4,4'-dichlorobenzhydrol (Aldrich Chemical Co.). Nmr δ 7.24 (s, 8), 5.71 (s, 1), and 2.32 (s, 1); ir 3450 (bm), 1600 (m), 1487 (s), 1400 (m), 1165 (m), 1087 (vs), and 1012 cm^{-1} (vs).

Thermal stability of phenyl oxalate

A quantity of 83 mg of phenyl oxalate[a] was heated in a nitrogen atmosphere at 350° for 0.5 hr. A weight loss of only 1 mg occurred, and the ir spectrum of the product was identical with that of starting material.

Pyrolysis of benzyl benzhydryl oxalate

A sample (Run 1) of 0.068 gm (0.196 mmole) of benzyl benzhydryl oxalate in 0.50 gm (2.94 mmole) of purified phenyl ether was degassed 3 times under vacuum and sealed at ~0.1 mm pressure in one half of a 15x125 mm pyrex test tube. The tube was heated at 245° for 11.5 hr in a bath containing Dow Corning 550 silicone fluid; when cool, the tube was opened, and 0.0156 gm (0.0928 mmole) of diphenylmethane[1] (Distilla-Products Industries) and 0.0164 gm (0.0781 mmole) of benzil (Matheson Coleman and Bell) were added as internal standards for nmr and glpc analysis, respectively. Components of the pyrolysate were identified by nmr and glpc peak enhancement. The identities of 4 or 5 compounds present in small quantities were not ascertained.

Another sample (Run 2) of 0.0723 gm (0.209 mmole) of benzyl benzhydryl oxalate in 0.50 gm (2.94 mmole) of purified phenyl ether was similarly degassed and sealed under vacuum and then heated at 235° for 89 hr; when cool, 0.0145 gm (0.0690 mmole) of benzil was added as an internal standard. Analysis measurements are given in Table 22.

Table 22. Analysis of the pyrolysate of benzyl benzhydryl oxalate in phenyl ether

Compound R	Area R Run 1[a]	Area R Run 2[b]
Toluene	0.07	0.22
Benzil[c]	0.99	1.36
1,1,2-Triphenylethane	0.30	0.70
Benzyl diphenylacetate	0.49	1.28
1,1,2,2-Tetraphenylethane	0.48	0.79
-Carbobenzoxy[d]	128	113
Toluene[d]	20	30

[a] Heated at 245° for 11.5 hr.

[b] Heated at 235° for 89 hr.

[c] Internal standard.

[d] Determined by nmr.

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[1] Diphenylmethane was not a product of pyrolysis.

Pyrolysis of benzyl oxalate

After 0.0598 gm (0.213 mmole) of benzyl oxalate, dissolved in 0.52 gm (3.06 mmole) of phenyl ether, degassed 3 times, and sealed under vacuum, was heated at 235 - 240° for 89 hr, a small amount of yellow crystals which were insoluble in phenyl ether even at ~200° (polybenzyl?) was noted in the pyrolysis tube. When cool, the tube was opened, and 0.0161 gm (0.0958 mmole) of diphenylmethane was added as an internal standard. By nmr analysis the area of the benzylic protons from benzyl oxalate at 5.00δ was 0.5 (188); the area for diphenylmethane methylene protons at 3.80δ was 52. Only traces of peaks at 3.95 and 2.10δ were observed.

Pyrolysis of methyl benzhydryl oxalate

Samples of methyl benzhydryl oxalate were pyrolyzed in the gas phase pyrolysis apparatus under the conditions in Table 23. After each sample had passed through the pyrolysis column (1-2 hr), the column was cooled to room temperature and washed with chloroform. The chloroform was stripped off, and each pyrolysate was then analyzed by nmr. Characteristic nmr peaks of the major components of the pyrolysate and their integration areas are presented in Table 24. Product identification was made by nmr and glpc peak enhancement with authentic samples; benzophenone, which could not be distinguished from benzhydrol by glpc analysis and which may or may not be visible in the nmr spectra, was found as a result of its characteristic carbonyl absorption at 1655 cm^{-1} in the ir spectrum. Appreciable decomposition of the neat oxalate does not occur below 250°. A typical nmr spectrum used for analysis is shown in Figure 2.

Table 23. Conditions for gas phase pyrolysis of samples of methyl benzhydryl oxalate

Run	Amount of oxalate, mmole	Column temperature, °C.	Pressure, mm
1	0.394	400[a]	0.07
2	0.370	400[b]	3.1
3	0.378	400[b]	2.4
4	0.285	450[a]	2.2
5	0.277	500[a]	2.2
6	0.378	560[a]	0.08

[a] The tube containing starting material was heated at 135°.

[b] The tube containing starting material was heated at 160°.

Table 24. Analyses of methyl benzhydryl oxalate pyrolysates

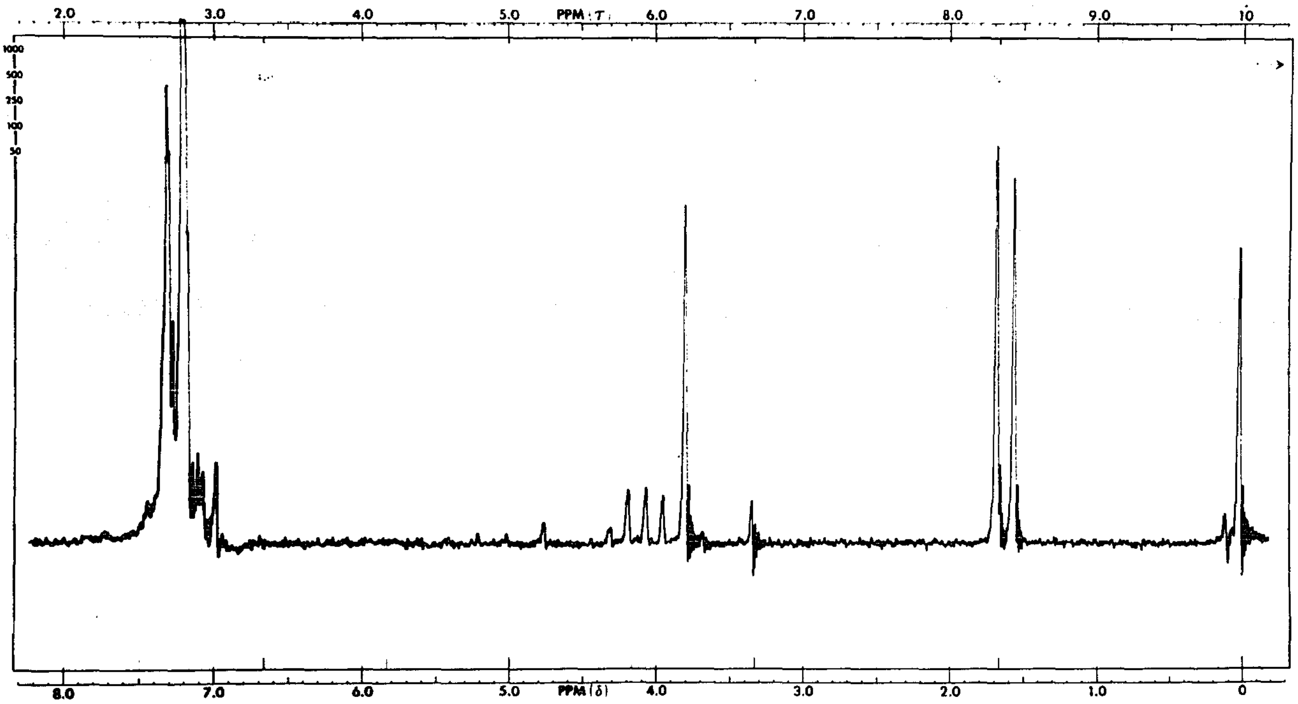
Compound R	Characteristic nmr peak, δ	Integration area R Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
1,1,2,2-Tetraphenylethane	4.66	--	trace	6[a]	45[a]	105[a]	21[a]
Diphenylmethane	3.94	--	--	trace	12[a]	39[b],59[a]	11[c],16[a]
Methyl benzhydryl oxalate	3.84	122	50	37	101	15	66
Methyl diphenylacetate	3.69	--	--	--	--	3	--
Methyl benzhydryl ether	3.36	20	3.5	6	35	22	9
1,1-Diphenylethane	1.62	--	--	1.5	18	204	172

[a] Corrected to 3 H by multiplying integration area by 1.5.

[b] Total integration area is 107, but 0.333 (204) or 68 is from the methinyl proton quartet of 1,1-diphenylethane.

[c] Total integration area is 68, but 0.333 (172) or 57 is from the methinyl proton quartet of 1,1-diphenylethane.

Figure 2. Pyrolysate of methyl benzhydryl oxalate (560° at 0.08 mm)


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
1000
500
250
100
50
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

Estimation of the rate constant for the decomposition of methyl tritylazocarboxylate

Nitrogen was bubbled for 3 min through a solution of 0.0203 gm (0.067 mmole) of methyl tritylazocarboxylate dissolved in 0.5 ml of benzene in an nmr tube. The solution was heated at 60° under nitrogen. The decomposition was followed by observing the disappearance of the methyl absorption at 3.86δ in the nmr spectrum as in Table 25.

Table 25. Decomposition of methyl tritylazocarboxylate in benzene at 60°

Time, min	Integration area of methyl group
0	114
30	44
300	~5[a]

[a] Considered to be infinity point absorption.

Analysis of the gases evolved (31) during the thermal decomposition of methyl tritylazocarboxylate in benzene

The total volume of the system--flask, condenser, and capillary tubing--in which the decomposition was carried out was 42 ml. The system was flushed with nitrogen for 45 min before 4.02 gm (12.2 mmole) of methyl tritylazocarboxylate dissolved in enough benzene to make 24 ml of solution was added to the flask. Nitrogen was then bubbled through the solution for 20 min. The solution was then heated at 60° for 3 hr, and the gas evolved was collected under a beaker submerged in a water tank. The collected gas was placed in a funnel submerged in a large water tank (capacity of 50 gal), and approximately 100 ml of the gas was transferred to a 100-ml gas burette; the volume, temperature, and pressure were recorded. The gas then was transferred to a Hemple pipette containing 30% aqueous potassium hydroxide to remove carbon dioxide; the remaining gas was transferred back to the gas burette, and the new volume was recorded. This transfer was repeated until no further decrease in volume was noted. Transfer of the gas to another Hemple pipette containing freshly prepared ammoniacal cuprous chloride removed carbon monoxide; the residual gas was returned to the gas burette, and the residual volume was recorded. This transfer was repeated until no further decrease in volume was noted. The residual gas was assumed to be nitrogen. The pertinent data are recorded in Table 26.

Table 26. Analysis of gases produced by decomposition of methyl tritylazocarboxylate

Gas	Temperature, °K	Pressure, mm[a]	Volume, ml[b,c]
Carbon dioxide	298	714	0.00
Carbon monoxide	298	714	2.00[d,e]
Nitrogen	298	714	90.00[e]

[a] Barometer and water vapor corrections have been applied.

[b] Total volume collected was 295 ml.

[c] Volume of the sample analyzed was 92.00 ml.

[d] Maximum volume of carbon monoxide present.

[e] Final volume after treatment with ammoniacal cuprous chloride was 101 ml, due to the presence of ammonia vapor which was not removed; correction for volume of ammonia was estimated to be 11 ml on the basis of gas analysis data for the decomposition of phenyl tritylazocarboxylate (p. 100).

Examination of the decomposition of methyl tritylazocarboxylate by esr

An esr tube containing a deoxygenated solution of 20 mg (0.06 mmole) of methyl tritylazocarboxylate in 0.2 ml of benzene under a nitrogen atmosphere was heated at 60° for 2 hr. After three dilutions with deoxygenated benzene, the esr spectrum could be measured. A spectrum of 18 lines having a coupling constant of ~1.4 gauss was obtained and was further resolved into 18 groups of four closely spaced hyperfine structure lines. The spectrum was identical to that published (51) for the trityl radical.

Separation and identification of the nonvolatile decomposition products from methyl tritylazocarboxylate in benzene

The benzene was stripped from the benzene solution of nongaseous products obtained from the decomposition of the 4.02 gm (12.2 mmole) of methyl tritylazocarboxylate used for the gas analysis experiment (*vide supra*). The crude products were dissolved in ~25 ml of dichloromethane and applied with a syringe to seven 8x20 cm glass plates coated with a 1 mm thickness of silica gel PF$_{254+366}$ (E. Merck Darmstadt). The plates were developed with hexane, 50% hexane--50% benzene, and benzene, a total of 20 times per plate. Each plate was divided into 4 bands (at least 20 bands were visible); each band was vacuumed into a Soxhlet thimble and was extracted with ~250 ml of ethyl acetate for 7 hr in a Soxhlet extractor. The ethyl acetate was stripped off under aspirator pressure.

Band no. 1 yielded 0.62 gm (2.54 mmole or 21 mole%) of triphenylmethane (mp 92 - 94°). Mp, glpc retention time, and nmr and ir spectra were identical to those of authentic triphenylmethane (Matheson Coleman and Bell).

When band no. 2 (1.43 gm) was treated with hot hexane, most of the solid did not dissolve. This material, when recrystallized from a mixture of hexane--dichloromethane, gave 0.87 gm (2.88 mmole or 24 mole%) of a crystalline compound which had the same mp (182 - 184°), glpc retention time, nmr spectrum, and ir spectrum as authentic methyl triphenylacetate prepared by a different route (p. 73).

When the hot hexane solution was allowed to cool, 0.41 gm (1.36 mmole or 11 mole%) of methyl 4-benzhydrylbenzoate (mp 78 - 79°; lit (67) mp 78 - 79°) crystallized. Nmr δ 7.95 (d, 2), 7.21 (m, 12), 5.57 (s, 1), and 3.85 (s, 3); ir 1716 (vs), 1610 (m), 1600 (m), 1492 (m), 1450 (m), 1435 (m), 1413 (w), 1277 (vs), 1115 (s), 1105 (s), 1075 (w) 1017 (m), 967 (w), and 880 cm^{-1} (w).

Band no. 4 (0.56 gm) contained small amounts of many compounds and was not further examined. Band no. 3 (0.83 gm) was again dissolved in dichloromethane, applied to three 8x20 cm plates coated with a 1 mm thickness of silica gel, developed in 50% hexane--50% benzene 15 times, and divided into 5 bands. Each of the new bands was extracted with ethyl acetate, and the ethyl acetate was removed under aspirator pressure.

From band no. 3' was recrystallized 0.24 gm (0.80 mmole or 6.5 mole%) of methyl 4-carbomethoxytriphenylacetate (mp 133 - 134°). Nmr δ 7.95 (d, 2), 7.23 (m, 12), 3.87 (s, 3), and 3.77 (s, 3); ir 1718 (vs), 1607 (w), 1492 (w), 1433 (m), 1315 (m), 1277 (vs), 1110 (s), and 1010 cm^{-1} (m); MW (mass spectrum) 360 m/e.

Anal. Calcd for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59. Found: C, 76.39; H, 5.50.

Bands no. 1' (0.08 gm), no. 4' (0.26 gm), and no. 5' (0.07 gm) did not yield crystalline materials and could not be identified. Band no. 2' (0.11 gm) yielded a crystalline material for which no complete structural assignment could be made.

Analysis of thermal decomposition products from methyl tritylazocarboxylate by glpc

Samples of 0.0200 gm (0.0606 mmole) of methyl tritylazocarboxylate in 0.31 gm (4.0 mmole) of benzene (Run 1) and 0.0225 gm (0.0681 mmole) of methyl tritylazocarboxylate in 0.41 gm (3.4 mmole) of purified cumene[1] (Run 2) were degassed 3 times each and sealed under vacuum (0.1 mm). After heating at 60° for 9 hr and 7.5 hr, respectively, the tubes were opened, and benzil was added as an internal standard. The glpc peak areas of the only detectable products are given in Table 27. No methyl formate, methyl benzoate, methyl oxalate, methyl carbonate, or methyl 2-phenylisobutyrate were observed.

Analysis of the gases evolved (31) during the thermal decomposition of phenyl tritylazocarboxylate in benzene

The system in which the decomposition was allowed to occur consisted of a flask, a condenser, and capillary tubing totalling 44 ml in volume. Nitrogen was allowed to pass through the system for 45 min; 4.54 gm (11.6 mmole) of phenyl tritylazocarboxylate was dissolved in enough benzene to produce 26 ml of solution which was introduced into the flask.

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[1] Cumene (~100 gm) was shaken with fresh portions of concentrated sulfuric acid (7) until only a light yellow color remained after shaking. The cumene was then washed with equal volumes of water, saturated sodium bicarbonate, and water and was dried over magnesium sulfate. Following distillation from sodium through a 50 cm column filled with glass helices, the cumene (bp 152 - 153°) was stored in a brown bottle in the dark.

Table 27. Products from the thermal decomposition of methyl trityl-azocarboxylate

Compound R	Area R Run 1[a]	 Run 2[b]
Triphenylmethane	0.46	2.43
Benzil[c]	2.03	9.70
Methyl triphenylacetate	0.70	3.91
Methyl 4-benzhydrylbenzoate	0.49	1.91
Methyl 4-carbomethoxytriphenylacetate	0.10	0.55

[a] In benzene as solvent.

[b] In cumene as solvent.

[c] Internal standard; 0.0610 mmole added to both Runs.

The reaction mixture was deoxygenated by bubbling nitrogen into the solution for 20 min. After deoxygenation, the decomposition was brought about by heating the solution at 75° for 3 hr, the gas evolved being collected under a beaker submerged in a water tank. Conventional gas analysis as previously described (p. 95) was utilized to quantitatively determine the amount of carbon dioxide collected by absorption in 30% potassium hydroxide and the amount of carbon monoxide in the sample by absorption in ammoniacal cuprous chloride. The residual gas was assumed to be nitrogen. The gas analysis conditions are tabulated in Table 28.

Table 28. Analysis of the gases produced by decomposition of phenyl tritylazocarboxylate

Gas	Temperature, °K	Pressure, mm[a]	Volume, ml[b,c]
Carbon dioxide	298	713	0.10
Carbon monoxide	298	713	2.20[d,e]
Nitrogen	298	713	96.50[e]

[a] Barometer and water vapor corrections have been applied.

[b] Total volume collected was 280 ml.

[c] Volume of sample analyzed was 98.80 ml.

[d] Maximum volume of carbon monoxide present.

[e] Final volume after treatment with ammoniacal cuprous chloride was ~ 108 ml, due to presence of ammonia vapor; addition of a small amount of hydrochloric acid to the water in the leveling bulb removed the ammonia and reduced the volume by 11 ml.

Examination of the decomposition of phenyl tritylazocarboxylate by esr

A deoxygenated solution of 8 mg (0.02 mmole) of phenyl tritylazocarboxylate in 0.2 ml of benzene was heated in an esr tube under a nitrogen atmosphere at 75° for 2 hr. An esr spectrum of 18 lines having a coupling constant of ~1.4 gauss was observed and was further resolved into 18 groups of four closely spaced hyperfine structure lines. This spectrum is exactly the same as the spectrum of the trityl radical (51).

Separation and identification of the nonvolatile decomposition products from phenyl tritylazocarboxylate in benzene

The benzene solution of nongaseous products obtained from the decomposition of the 4.54 gm (11.6 mmole) of phenyl tritylazocarboxylate used for the gas analysis experiment (vide supra) was evaporated to dryness. The crude products, dissolved in ~25 ml of dichloromethane, were applied with a syringe to eight 8x20 cm glass plates coated with a 1 mm thickness of silica gel $PF_{254+366}$ (E. Merck Darmstadt). Each plate was developed about 20 times with hexane, 50% hexane--50% benzene, and benzene. Each plate was divided into 6 bands (at least 20 were visible); each band was vacuumed into a Soxhlet thimble and was extracted with ~250 ml of ethyl acetate for at least 7 hr in a Soxhlet extractor. Each band extract was evaporated to dryness in a rotary evaporator.

From band no. 1 0.52 gm (2.13 mmole or 18 mole%) of triphenylmethane (mp 92 - 94°) was isolated. Authentic triphenylmethane (Matheson Coleman and Bell) had the same mp, glpc retention time, and nmr and ir spectra as band no. 1.

The material from band no. 2 was recrystallized from hexane to yield 0.48 gm (1.32 mmole or 11 mole%) of phenyl triphenylacetate (mp 124 - 125°). The mp, glpc retention time, and nmr and ir spectra were identical to those of phenyl triphenylacetate prepared by a different route (p. 74).

Band no. 3 by nmr analysis contained a mixture of phenyl triphenylacetate and phenyl 4-benzhydrylbenzoate (see band no. 4) amounting to 0.45 gm (1.24 mmole or 11 mole%).

Upon recrystallization of band no. 4 from hexane 0.69 gm (1.24 mmole or 11 mole%) of phenyl 4-benzhydrylbenzoate (mp 125 - 126°) was obtained. Nmr δ 8.15 (d, 2), 7.23 (m, 17), and 5.63 (s, 1); ir 1725 (vs), 1595 (m), 1493 (s), 1445 (w), 1408 (w), 1263 (vs), 1160 (s), 1073 (s), 1017 (m), 1000 (w), 913 (w), and 878 cm^{-1} (w); MW (mass spectrum) 364 m/e.

Anal. Calcd for $C_{26}H_{20}O_2$: C, 85.70; H, 5.50. Found: C, 85.35; H, 5.74.

Band no. 6 (0.35 gm) was a mixture of many highly colored bands; no further separation was attempted. Band no. 5 (0.94 gm) was redissolved in dichloromethane, applied to three 8x20 cm plates coated with a 1 mm thickness of silica gel, developed in 50% hexane--50% benzene 15 times, and divided into 5 bands. Each of these new bands was extracted with ethyl acetate, and the ethyl acetate was removed from each band by rotary evaporation.

From band no. 3' was isolated by recrystallization from hexane--dichloromethane 0.18 gm (0.372 mmole or 3.2 mole%) of 4,4'-dicarbophenoxytriphenylmethane (mp 151 - 153°). Nmr δ 8.16 (d, 4), 7.25 (m, 19), and 5.70 (s, 1); ir 3010 (w), 1733 (vs), 1610 (m), 1595 (m), 1495 (s), 1415 (m), 1265 (vs), 1176 (vs), 1160 (s), 1074 (vs), 1017 (s), 1000 (w), 924 (m), 876 (w), and 847 cm^{-1} (m).

Band no. 1' (0.01 gm) was too small to obtain any positive information. Bands no. 2' (0.24 gm), no. 4' (0.28 gm), and no. 5' (0.11 gm) yielded crystalline products upon recrystallization from hexane--dichloromethane, but complete structural assignments could not be made for these compounds.

Pyrolysis of benzyl triphenylacetate

Solutions as in Table 29 of benzyl triphenylacetate in phenyl ether, biphenyl, 1,3,5-triisopropylbenzene, or n-hexadecane were degassed 3 times, sealed under vacuum, and heated at 350°; after cooling the tubes were opened, and benzil was added as an internal standard. The pyrolysis in n-hexadecane was impossible to analyze in any detail; at least 25 products were visible in the glpc trace of this pyrolysate. The largest peak was due to triphenylmethane, and its yield is estimated to be $< 10\%$. The glpc areas of the major detectable products in the other pyrolysates are listed in Tables 30, 31, and 32. Small amounts of other compounds were observed; two of these compounds may be present--tritanol, tetraphenylmethane, or 9-phenylfluorene. Benzaldehyde, benzyl trityl ether, 1,1,1,2-tetraphenylethane, and starting material are definitely absent from the pyrolysates.

Analysis of the gases evolved (31) during the pyrolysis of benzyl triphenylacetate in phenyl ether at 350°

A total of 0.7509 gm (1.99 mmole) of benzyl triphenylacetate dissolved in 6.53 gm (38.4 mmole) of phenyl ether (Run 1) was placed in 2 thick-walled tubes and was degassed 3 times and sealed under vacuum. The tubes were heated at 350° for 32 hr. After cooling the tubes were broken open under a funnel submerged in a large water tank (capacity of 50 gal). The combined trapped gas from both tubes was transferred to the gas analysis apparatus previously described (p. 95) and was analyzed using 30% potassium hydroxide for absorption of any carbon dioxide present and ammoniacal cuprous chloride for absorption of any carbon monoxide present.

A total of 0.7560 gm (2.00 mmole) of benzyl triphenylacetate dissolved in 6.15 gm (36.2 mmole) of phenyl ether (Run 2) was pyrolyzed and analyzed as above. The data are recorded in Table 33.

Table 29. Samples of benzyl triphenylacetate pyrolyzed at 350°

Run	Amount of ester, mmole	Amount of solvent, mmole	Amount of benzil,[a] mmole	Period of heating, hr
1	0.149	2.40[b]	0.0867	30
2	0.0925	1.88[b]	0.0733	36
3	0.101	1.95[b]	0.0871	49
4	0.0952	1.88[b]	0.0833	91
5	0.0312	0.71[b,c]	0.0391	48
6	0.0860	1.65[d]	0.0719	36
7	0.105	1.76[d]	0.0653	57
8	0.121	1.82[d]	0.0662	57
9	0.0947	1.53[d]	0.0842	91
10	0.132	1.57[e]	0.103	30
11	0.0958	1.57[e]	0.0976	49
12	0.0868	1.67[e]	0.0895	65

[a] Internal standard.

[b] Biphenyl.

[c] The sample contained 12.5 µl of methanol.

[d] Phenyl ether.

[e] 1,3,5-Triisopropylbenzene.

Table 30. Analyses of samples of benzyl triphenylacetate pyrolyzed in biphenyl at 350°

Compound R	Area R Run 1[a]	Run 2[a]	Run 3[b]	Run 4[a]	Run 5[a]
Toluene	21[c]	0.23	0.48	0.27	0.21
Diphenylmethane	83[c]	0.85	1.55	0.95	--
Benzil[d]	3.22	1.45	2.79	1.63	2.61
Benzophenone	2.66	0.98	1.79	1.05	0.78
Triphenylmethane	2.26	0.74	1.41	0.80	1.00
Unknown[e]	0.50	0.16	0.29	0.17	--

[a] Only 1 injection.

[b] Average of 2 injections.

[c] Nmr integration area.

[d] Internal standard.

[e] Tritanol, tetraphenylmethane, or 9-phenylfluorene.

Table 31. Analyses of samples of benzyl triphenylacetate pyrolyzed in phenyl ether at 350°

	Area R			
Compound R	Run 6[a]	Run 7[b]	Run 8[c]	Run 9[a]
Toluene	48;[e] 0.26	--	0.59	80;[e] 0.48
Unknown A[d]	0.26	--	0.28	0.17
Diphenylmethane[e]	127	41	75	58
Benzil[f]	1.71	4.42	3.45	1.99
Benzophenone	1.17	3.34	2.95	0.79
Triphenylmethane	1.02	26;[e] 3.22	43;[e] 2.97	1.30
Unknown B[g]	0.14	0.64	0.45	0.19

[a] Only 1 injection.

[b] Average of 2 injections.

[c] Average of 3 injections.

[d] Not phenol.

[e] Nmr integration area.

[f] Internal standard.

[g] Tritanol, tetraphenylmethane, or 9-phenylfluorene.

Table 32. Analyses of samples of benzyl triphenylacetate pyrolyzed in 1,3,5-triisopropylbenzene at 350°

Compound R	Area R Run 10[a]	 Run 11[b,c]	 Run 12[b]
Toluene	--	0.96	0.43
Diphenylmethane	--	2.02	0.72
Benzil[d]	5.11	3.46	1.35
Benzóphenone	1.67	1.13	0.37
Triphenylmethane	3.49	2.33	0.84

[a] Only 1 injection.

[b] Average of 2 injections.

[c] Not all of the standard, benzil, dissolved; therefore, results may be high.

[d] Internal standard.

Table 33. Data for gases produced during the pyrolysis of benzyl triphenylacetate

Gas	Temperature, °K Run 1	 Run 2	Pressure, mm[a] Run 1	 Run 2	Volume, ml Run 1[b]	 Run 2[c]
Carbon dioxide	300	301	708	707	10.90[d]	9.00
Carbon monoxide	300	301	708	707	28.00	28.40

[a] Barometer and water vapor corrections have been applied.

[b] Residual volume was 2.50 ml.

[c] Residual volume was 1.40 ml.

[d] Due to a reading error, this value should probably be 9.90 ml.

Pyrolysis of benzyl trityl ether

As in Table 34, samples of benzyl trityl ether in biphenyl which were degassed and sealed under vacuum were heated at 350°. The pyrolysates were cooled, opened, and analyzed by glpc, using diphenylmethane (shown not to be a product) as the internal standard. The glpc areas of the major detectable products are presented in Table 35. Small amounts of two unidentified compounds which might be tritanol, tetraphenylmethane, or 9-phenylfluorene were also noted.

Table 34. Samples of benzyl trityl ether pyrolyzed at 350°

Run	Amount of ether, mmole	Amount of biphenyl, mmole	Amount of DPM,[a,b] mmole	Period of heating, hr
1	0.0937	1.56	0.0888	22
2	0.101	1.56	0.0958	22
3	0.0954	1.56	0.0732	35
4	0.107	1.49	0.0953	35

[a] DPM--diphenylmethane.

[b] Internal standard.

Table 35. Analyses of samples of benzyl trityl ether pyrolyzed at 350°

Compound R	Run 1[a]	Area R Run 2[b]	Run 3[b]	Run 4[b]
Benzaldehyde	0.66	0.88	0.56	0.48
Diphenylmethane[c]	1.55	1.88	1.00	1.20
Triphenylmethane	2.18	2.62	1.81	1.81

[a] Only 1 injection.

[b] Average of 2 injections.

[c] Internal standard.

Pyrolysis of trityl phenylacetate

All samples in this experiment were dissolved in biphenyl, degassed 3 times, and sealed under vacuum; after heating the samples were opened, and benzil was added as an internal standard, as in Table 36. The glpc areas of the major detectable peaks are listed in Table 37. Small amounts of unidentified compounds and a trace quantity of toluene were observed. The starting material decomposes on passage through the SE-30 column under the conditions necessary to push it through in a reasonable length of time.

Pyrolysis of methyl triphenylacetate

A sample of 0.0307 gm (0.102 mmole) of methyl triphenylacetate in 0.34 gm (2.00 mmole) of phenyl ether was degassed 3 times, sealed under vacuum, and heated at 350° for 10 days. After cooling the tube was opened, and 0.0149 gm (0.0710 mmole) of benzil was added as an internal standard. The glpc peak areas of the major detectable products are presented in Table 38. Only unidentified traces of other compounds were observed.

Table 36. Samples of trityl phenylacetate pyrolyzed

Run	Amount of ester, mmole	Amount of benzil,[a] mmole	Temperature, °C	Period of heating, hr
1[b]	0.0995	0.0771	295	12
2[b]	0.0986	0.103	260	62
3[b]	0.0905	0.0743	235	122
4[c]	0.115	0.0700	230	240

[a] Internal standard.

[b] Solvent--biphenyl (1.49 mmole).

[c] Solvent--biphenyl (1.56 mmole).

Table 37. Analyses of samples of trityl phenylacetate pyrolyzed

		Area R[a]		
Compound R	Run 1	Run 2	Run 3	Run 4
Diphenylmethane	0.37	0.13	0.07	0.15
Benzil[b]	2.03	1.82	1.53	2.67
Benzophenone	0.66	0.40	0.40	0.89
Triphenylmethane	1.42	0.92	1.05	2.65
Unknown A	--	--	0.33	0.64
Unknown B	0.56	0.32	0.15	0.60

[a] Only 1 injection.

[b] Internal standard.

Table 38. Analysis of methyl triphenylacetate pyrolysate

Compound R	Area R[a]
Toluene	0.12
Benzil[b]	1.82
Benzophenone	0.26
Triphenylmethane	1.66

[a] Average of 2 injections.

[b] Internal standard (0.0710 mmole).

Pyrolysis of phenyl triphenylacetate

A solution of 0.0448 gm (0.123 mmole) of phenyl triphenylacetate in 0.36 gm (2.12 mmole) of phenyl ether was degassed 3 times, sealed under vacuum, and heated at 350° for 10 days. After cooling the tube was opened, and 0.0160 gm (0.0762 mmole) of benzil was added as an internal standard. The glpc areas of the major detectable products are listed in Table 39. Only unidentified traces of other compounds were observed.

Table 39. Analysis of phenyl triphenylacetate pyrolysate

Compound R	Area R[a]
Phenol	1.00
Benzil[b]	1.74
Triphenylmethane	2.40

[a] Average of 2 injections.

[b] Internal standard (0.0762 mmole).

Kinetic studies on triphenylacetate esters

For each kinetic run a sample of an ester was dissolved in purified phenyl ether and divided into 10 approximately equal amounts in ten 15x125 mm pyrex test tubes. After three degassing operations the ten tubes were sealed at 0.1 mm pressure and then heated in the aluminum block constant temperature apparatus held at 350°. Periodically a tube was removed and cooled to room temperature. The rate of the decomposition of these esters could be conveniently followed by measuring the disappearance of the ester carbonyl in the ir spectrum using phenyl ether in the reference cell. The rate of decomposition of the benzyl ester could also be determined from the rate of formation of benzophenone by measuring the growth of the characteristic benzophenone carbonyl in the ir spectrum. The rate data are presented in Tables 40-46. The kinetic plot from the data in Table 41 is shown in Figure 3.

Table 40. Decomposition of benzyl triphenylacetate in phenyl ether at 350° (Run 1)

Time, min	Absorbance, A[a,b]	% A
0	0.498	100
60	0.441	88.5
150	0.320	64.3
236	0.306	61.5
330	0.208	41.6
453	0.146	29.3
660	0.068	13.7
∞	0.000	--

[a] Corrected for infinity point absorbance.

[b] Original amount of ester was 0.381 mmole in 19.8 mmole of phenyl ether.

Table 41. Decomposition of benzyl triphenylacetate in phenyl ether at 350° (Run 2)

Time, min	Absorbance, A[a,b]	%A
0	0.640	100
75	0.538	84.0
152	0.429	67.0
224	0.332	51.9
315	0.244	38.1
554	0.122	19.1
∞	0.000	--

[a] Corrected for infinity point absorbance.

[b] Original amount of ester was 0.507 mmole in 19.7 mmole of phenyl ether.

Table 42. Formation of benzophenone from benzyl ester at 350° (Run 1)

Time, min	Absorbance, A	A_t[a]	$\frac{A_\infty - A_t}{A_\infty}$
0	0.006	0.000	1.00
60	0.050	0.044	0.869
150	0.124	0.118	0.649
236	0.173	0.167	0.503
330	0.225	0.219	0.348
453	0.263	0.257	0.235
660	0.311	0.305	0.092
∞	0.342[b]	0.336	--

[a] Absorbance at time t, A_t, equals absorbance, A, less absorbance at time zero, A_o.

[b] Absorbance at time infinity, A_∞.

Table 43. Formation of benzophenone from benzyl ester at 350° (Run 2)

Time, min	Absorbance, A	A_t[a]	$\frac{A_\infty - A_t}{A_\infty}$
0	0.006	0.000	1.00
75	0.093	0.087	0.791
152	0.183	0.177	0.575
224	0.233	0.227	0.456
315	0.299	0.293	0.298
554	0.363	0.357	0.144
∞	0.423[b]	0.417	--

[a] Absorbance at time t, A_t, equals absorbance, A, less absorbance at time zero, A_o.

[b] Absorbance at time infinity, A_∞.

Table 44. Decomposition of methyl triphenylacetate[a] in phenyl ether at 350°

Time, min	Absorbance, A	Corrected A[b]	% A
0	--	0.710[c,d]	100
260	0.620	0.610	86.0
480	0.636	0.626	88.2
1440	0.515	0.505	71.2
2550	0.374	0.364	51.3
2880	0.303	0.293	41.3
4080	0.243	0.233	32.8
4620	0.206	0.196	27.6
5280	0.167	0.157	22.1
5940	0.136	0.126	17.8
∞	0.010	--	--

[a] This ester was not very soluble in phenyl ether and tended to sublime.

[b] Corrected for infinity point absorbance.

[c] Original amount of ester was 0.601 mmole in 2.37 mmole of phenyl ether.

[d] Value was obtained by extrapolation to zero time.

Table 45. Decomposition of phenyl triphenylacetate in phenyl ether at 350° (Run 1)

Time, min	Absorbance, A	Corrected A[a]	%A
0	0.690	0.679[b]	100
240	0.647	0.636	93.8
720	0.550	0.539	79.4
1395	0.536	0.525	77.4
1575	0.513	0.502	74.0
2160	0.409	0.398	58.7
2880	0.385	0.374	55.2
3600	0.322	0.311	45.9
4320	0.274	0.263	38.8
5265	0.225	0.214	31.6
∞	0.011	--	--

[a] Corrected for infinity point absorbance.

[b] Original amount of ester was 0.606 mmole in 23.8 mmole of phenyl ether.

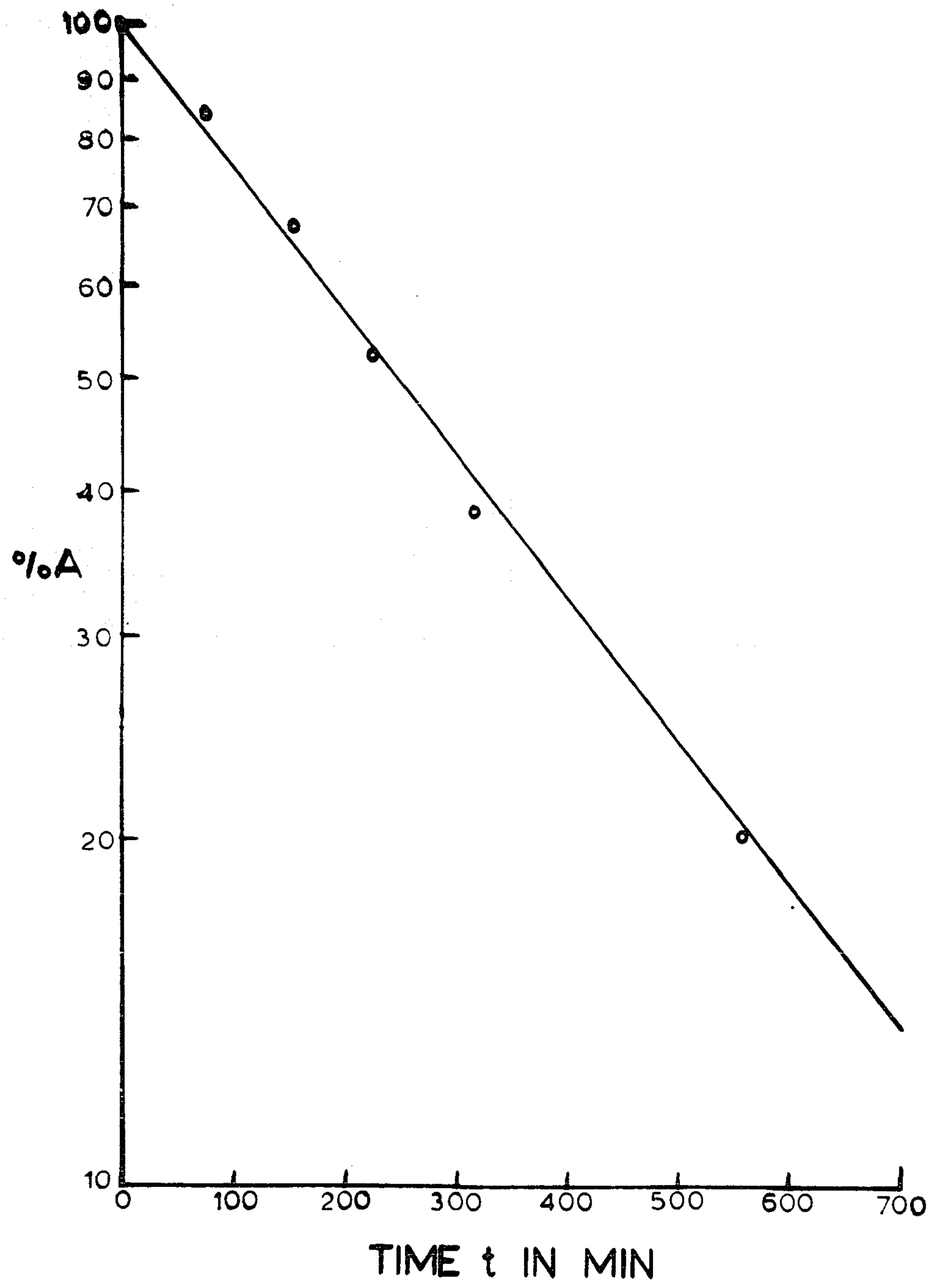
Table 46. Decomposition of phenyl triphenylacetate in phenyl ether at 350° (Run 2)

Time, min	Absorbance, A	Corrected A[a]	%A
0	0.699	0.688[b]	100
645	0.596	0.585	85.0
1395	0.535	0.524	76.2
2280	0.446	0.435	63.3
2830	0.423	0.412	59.9
4005	0.349	0.338	49.2
4380	0.324	0.313	45.5
5175	0.272	0.261	38.0
6705	0.206	0.195	28.4
∞	0.011	--	--

[a] Corrected for infinity point absorbance.

[b] Original amount of ester was 5.99 mmole in 23.7 mmole of phenyl ether.

Figure 3. Kinetic plot for the decomposition of benzyl triphenylacetate in phenyl ether at 350° (Run 2)


100
90
80
70
60
50
40
30
20
10
%A
0
100
200
300
400
500
600
700
TIME t IN MIN

SUMMARY

Studies of the pyrolyses of benzhydryl oxalates, symmetrical and unsymmetrical, indicate that the initial decomposition step involves the concerted, homolytic cleavage of one alkyl--oxygen bond and the central carbon--carbon bond. Detection of benzyl and benzhydryl diphenylacetates in the pyrolysates of benzyl benzhydryl oxalate and benzhydryl oxalate, respectively, can only be explained if the existence of benzoxycarbonyl and benzhydroxycarbonyl radicals is allowed. Although the results of labelling experiments show that the major source of these ester products is from an intramolecular recombination of radicals, apparently a small portion of these radicals can escape from the solvent cage to react intermolecularly. From pyrolysis of methyl benzhydryl oxalate in the gas phase it is seen that decarboxylation of the methoxycarbonyl radical is favored at 400° but at higher temperatures decarboxylation becomes the favored process.

A convenient method for generating alkoxycarbonyl radicals from tritylazocarboxylate esters has been discovered; compared to the related alkylcarboxy radicals which have proved to be very unstable, alkoxycarbonyl radicals are relatively stable species. These radicals can escape from a solvent cage and before decarboxylation or decarbonylation can attack radical species in solution other than themselves; alkoxycarbonyl radicals are unreactive radicals because aromatic solvents such as benzene are not attacked and active hydrogen-atom donating solvents such as cumene do not act as hydrogen-atom donors.

The most startling result of the pyrolyses of triphenylacetates is the observation that equal amounts of benzophenone, diphenylmethane, and carbon monoxide are formed from benzyl triphenylacetate. Formally, a phenyl migration from the triphenylmethyl group to the benzyl group must occur to give rise to these products; apparently, this decomposition requires the intervention of a short-lived diphenyl α-lactone species.

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