Organic Oxalates. I. Thermal Decomposition of Benzhydryl Oxalates[1a]

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Products of the thermal decomposition of benzhydryl and 4,4′-dichlorobenzhydryl oxalates neat and in phenyl ether solutions were determined. Two main nonvolatile products are the corresponding tetraarylethane and benzhydryl diarylacetate. These product studies and other experimental results indicate that the initial decomposition step involves the concerted homolytic cleavage of one benzhydryl–oxygen bond and the central carbon–carbon bond. From labeling experiments it is shown that in phenyl ether solution the ethane arises mainly by an intermolecular path and the ester arises mainly by an intramolecular path.

Although the pyrolysis of esters[2] has been the subject of many studies, little attention has been paid to the products and nature of the pyrolytic decomposition of oxalate esters. About 1850, Malaguti[3] and Cahours[4] reported that pentachloroethyl oxalate and trichloromethyl oxalate decompose at 250–400° to give carbon monoxide and phosgene plus other products. Around 1900, several workers[5] found that ethyl oxalate decomposed thermally to give mainly carbon dioxide, carbon monoxide, and olefins. Tilicheev[6] pyrolyzed ethylene oxalate at 240° to yield 40% ethylene and carbon dioxide, 28% ethylene carbonate and carbon monoxide, and 24% ethylene glycol acetal of acetaldehyde. The decomposition of other cyclic oxalates was studied by Tilicheev.[7]

More recently, Montaudo and Purrello[8] studied the decomposition of neat benzyl oxalate at 280°. Unreproducible yields of benzyl alcohol, benzaldehyde, benzyl ether, bibenzyl, and polybenzyl were obtained. A radical process was postulated to account for the products.

Karabatsos, Corbett, and Krumel[9] recently studied the pyrolysis of oxalates that possess a β hydrogen and can thus undergo an elimination reaction to form olefins. Tertiary oxalates both neat and in quinoline solution decomposed readily at 140–160° to give 80–100% of the corresponding olefins, whereas primary and secondary oxalates were stable up to 325°. At temperatures above 210° formate esters were observed as products in addition to olefins. Since the composition of the olefin products was more like the mixture of isomers obtained from acid-catalyzed and dimethyl sulfoxide dehydration of alcohols rather than the mixture obtained from ester and xanthate pyrolyses, an ion-pair mechanism was suggested.

Consideration of the thermal decomposition of organic oxalates that contain no β hydrogens and hence cannot eliminate raises many questions. What effect does the structure of the organic moiety have on the mode of decomposition? If the mechanism of decomposition is free radical in nature, how many bonds cleave simultaneously? Does cage recombination occur? Does decarbonylation or decarboxylation tend to occur? How does the thermal decomposition of organic oxalates compare with that of the related diacyl peroxides? We report here our initial findings on the thermal decomposition of dibenzhydryl oxalates.[10] We anticipated that formation of the stable benzhydryl radical should favor decomposition by a radical path.

Results and Discussion

Benzhydryl and 4,4′-dichlorobenzhydryl oxalates readily decompose when heated above 200°. In Table I are presented the yields of products obtained from the decomposition of these oxalates neat and in phenyl ether solution. From these data, it is seen that the two main nonvolatile products are the corresponding tetraarylethane and benzhydryl diarylacetate obtained in a ratio of *ca.* 60:20. Careful scrutiny of the nuclear magnetic resonance (nmr) spectrum of the crude pyrolysate showed no benzhydrol. Since chromatography of the oxalate gave benzhydrol but chromatography of the ester gave no benzhydrol, the benzhydrol obtained from the chromatographic column must come

TABLE I

PRODUCTS OF PYROLYSIS OF BENZHYDRYL OXALATES

Phase	Temp, °C	Time, hr	[$(Ar_2CH)_2$], %	[$Ar_2CHCO_2CHAr_2$], %	[Ar_2CHOH],[a] %
			Benzhydryl Oxalate		
Neat[b]	275	0.5	57	21	7
Solution[c,d]	225	2	43, 41	10, 10	...
Solution[c–e]	225	10	62	16	...
Neat[d]	200	2	17, 20	16, 16	...
Neat[d,f,g]	225	1	5.3	6.3	...
Solution[c,f,h]	225	1	0	0	...
			4,4′-Dichlorobenzhydryl Oxalate		
Neat[b]	275	0.5	55	27	9

[a] Benzhydrol comes from the hydrolysis of the oxalate during column chromatography; yield based on 2 moles of benzhydrol from each mole of oxalate. [b] Products were chromatographed and weighed. [c] 10% oxalate in phenyl ether. [d] Products were analyzed by nmr with diphenylmethane as an internal standard. [e] The material not accounted for is probably a result of reaction of the radicals with solvent.[10] [f] Pyrolysis was carried out in the presence of oxygen. [g] The major product (*ca.* 45%) was benzophenone; 5% benzhydryl ether was obtained. [h] Presumably benzophenone is the major product, but it could not be quantitatively determined by nmr because of the solvent phenyl ether.

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[2] C. H. Depuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

[3] M. J. Malaguti, *Ann. Chim.* (Paris), [3] **16**, 5 (1846).

[4] A. Cahours, *ibid.*, [3] **19**, 352 (1847).

[5] (a) C. Engler and J. Grimm, *Ber.*, **30**, 2923 (1897); (b) J. B. Senderens, *Compt. Rend.*, **146**, 1211 (1908).

[6] M. D. Tilicheev, *Ber.*, **56**, 2218 (1923).

[7] M. D. Tilicheev, *J. Russ. Phys. Chem. Soc.*, **58**, 447 (1927); *Chem. Abstr.*, **21**, 3358 (1927).

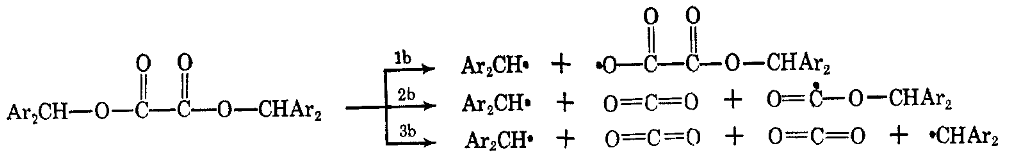
[8] G. Montaudo and G. Purrello, *Ann. Chim.* (Rome), **51**, 876 (1961).

[9] G. J. Karabatsos, J. M. Corbett, and K. L. Krumel, *J. Org. Chem.*, **30**, 689 (1965).

[10] During our investigation, we became aware of a related study of the thermolysis of benzhydryl oxalates by Professor J. Warkentin and D. M. Singleton. These workers carried out a kinetic study of the thermolysis of substituted benzhydryl oxalates. Our results are in good agreement (see ref 11).

[11] Warkentin reached this same conclusion from kinetic measurements.[10]

MECHANISMS 1b–3b



from hydrolysis of the oxalate on the column. In phenyl ether solution at 225°, the half-life of decomposition of the oxalate must be <2 hr.

Three reasonable mechanisms for the thermal decomposition of benzhydryl oxalate are homolytic cleavages to form a benzhydryl radical and an acyloxy radical (path 1b), a benzhydryl radical, one molecule of carbon dioxide, and an alkoxycarbonyl radical (path 2b), or two benzhydryl radicals and two molecules of carbon dioxide (path 3b). Obviously these three possible pathways involve one-bond, two-bond, or three-bond cleavages. Two results strongly indicate that the benzhydryl radical is produced. First, the yield of tetraphenylethane and benzhydryl diphenylacetate decreases drastically when the decomposition is carried out in the presence of oxygen, and benzophenone and benzhydryl ether are formed. It is well known that oxygen is an effective trap for alkyl radicals[12] and benzhydryl ether and benzophenone are reasonable products from the reaction. The possibility that oxygen is destroying tetraphenylethane and benzhydryl diphenylacetate after they are formed can be dismissed since at least 90% of the mixture of these two materials is recovered unchanged when subjected to pyrolysis conditions (225° for 1 hr) in the presence of oxygen. The second observation that supports the intermediacy of benzhydryl radicals is the finding by deuterium labeling (see below) that the tetraphenylethane is produced by an intermolecular process. Coupling of two free benzhydryl radicals most reasonably accounts for this result.

Since phenyl oxalate can be heated to 350° for 0.5 hr with only negligible decomposition, thermolysis of benzhydryl oxalate must initially involve cleavage of the benzhydryl–oxygen bond. Formation of the stable benzhydryl radical instead of the unstable phenyl radical accounts for the instability of the benzhydryl oxalate. Greater steric repulsion between the benzhydryl groups instead of the phenyl groups could not account for such a big stability difference. In addition to cleavage of the benzhydryl–oxygen bond, cleavage of the central carbon–carbon bond must occur simultaneously since benzhydryl diphenylacetate can be heated at 225° for 1.25 hr with essentially no decomposition. If only one-bond cleavage of benzhydryl oxalate occurs (path 1b), then benzhydryl diphenylacetate should cleave at approximately the same rate since the stability of the two acyloxy radicals and relief of steric repulsions during decomposition should be about the same. The central oxalate bond may be weak since it is joining two positively polarized atoms.[13]

Since a high yield of benzhydryl diphenylacetate is obtained from the decomposition of benzhydryl oxalate, concerted cleavage of three bonds (path 3b) is ruled out. Thus concerted cleavage of two bonds (path 2b) seems to be the initial step in the decomposition of benzhydryl oxalates.[11] Induced decomposition of the oxalate by benzhydryl radicals to form benzhydryl diphenylacetate is also ruled out since benzhydryl radicals were generated from *t*-butylperoxy diphenylacetate in the presence of benzhydryl oxalate in benzene solution and no benzhydryl diphenylacetate or significant loss of oxalate was observed.

In order to ascertain whether the formation of the two main products is inter- or intramolecular, we decomposed in phenyl ether a 50:50 mixture of benzhydryl oxalate and benzhydryl-α-d_1 oxalate. The isotope distributions of the two products were determined by mass spectral analysis. For both products, the $d_0/d_1/d_2$ ratio should be 50:0:50 for an intramolecular reaction and 25:50:25 for an intermolecular reaction. In Table II are presented the isotopic distributions of the two products.

TABLE II

ISOTOPIC DISTRIBUTION IN TETRAPHENYLETHANE AND BENZHYDRYL DIPHENYLACETATE PRODUCED DURING 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
Tetraphenylethane	24	45	31
Benzhydryl diphenylacetate	54	14	32

From these distributions, one must conclude that the tetraphenylethane is formed mainly by an intermolecular reaction and the benzhydryl acetate is formed mainly by an intramolecular reaction. However, these pathways cannot be the only mode of formation since the isotope distributions are not exactly those calculated for inter- and intramolecular reactions. 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. The inequality of the d_0 and d_2 peaks for the benzhydryl diphenylacetate may in part be a result of experimental error in measuring the magnitudes of the peaks since the molecular ion peaks were weak. Although mass spectral analyses were run at as low an ionization voltage as possible (17 ev), even at the lowest voltages fragmentations occurred. However, 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 were approximately constant from low to high ionization voltages.

Even though the exact isotopic distributions cannot be explained, it is clear that the tetraphenylethane comes mainly from an intermolecular reaction and the benzhydryl diphenylacetate comes mainly from an intramolecular reaction. This observation is readily explained 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 gives the ester from an intramolecular reaction. The stability of the benz-

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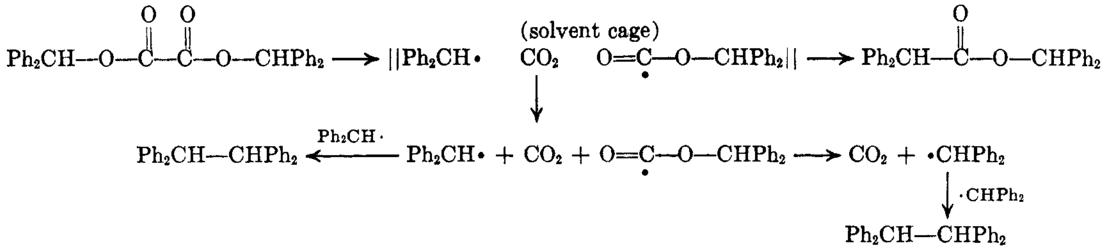
(12) G. A. Russell, *J. Chem. Educ.*, **36**, 111 (1959).

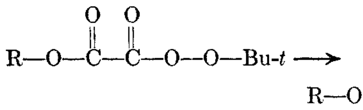
(13) P. D. Bartlett, B. A. Gontarev, and H. Sakurai, *J. Am. Chem. Soc.*, **84**, 3101 (1962).

Scheme I



hydroxycarbonyl radical must be great enough to be captured in the solvent cage, and it must be stable enough to diffuse out of the cage since a small amount of ester is formed intermolecularly. However, this radical must decompose to a benzhydryl radical and a molecule of carbon dioxide rather quickly since little ester forms intermolecularly. Thus the scheme shown in Scheme I accounts for the main portion of the thermolysis of benzhydryl oxalates in phenyl ether.

Alkoxycarbonyl radicals have been generated by the decomposition of alkyl *t*-butylperoxyoxalate by Bart-



$$\mathrm{R{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}O{-}Bu\text{-}\mathit{t}} \longrightarrow \mathrm{R{-}O{-}\underset{\bullet}{C}{=}O + CO_2 + \cdot O{-}Bu\text{-}\mathit{t}}$$

lett and co-workers.[12,14] Indeed, Bartlett and Bauld have generated benzhydroxycarbonyl radicals.[15] It is interesting that even the benzhydroxycarbonyl radical is stable enough to be trapped whereas the related benzhydrylcarboxy radical is so unstable that it probably never forms.[16]

The thermal decomposition of benzhydryl oxalates to tetraphenylethanes is also of synthetic interest since the oxalates can be prepared from readily available starting materials and the decomposition and work-up are convenient and uninvolved.

Experimental Section

Materials and Methods.—Equipment has been previously described.[17] All infrared spectra were taken using chloroform as the solvent. All nmr spectra were taken using deuteriochloroform as solvent and tetramethylsilane as an internal standard. Elemental analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Oxalic acid dihydrate was obtained from Baker Chemical Co. 4,4′-Dichlorobenzhydrol was obtained from Aldrich Chemical Co. Benzhydrol and thionyl chloride were obtained from Matheson Coleman and Bell. Diphenylacetic acid and diphenylmethane were obtained from Eastman Kodak Co. The nmr spectrum of the diphenylmethane showed peaks at δ 7.16 (singlet, 10 H) and 3.91 (singlet, 2 H). *t*-Butyl hydroperoxide was obtained from K and K Laboratories and purified as previously described.[17] Florisil (60–100 mesh) was obtained from E. H. Sargent and Co. Benzhydrol-α-d_1 was obtained by the reduction of benzophenone with lithium aluminum deuteride.[18] Phenyl ether obtained from Matheson Coleman and Bell was washed with aqueous sodium hydroxide and water, dried over magnesium sulfate, and distilled before use. Ligroin was distilled before use, bp 65–75°.

The oxalates were prepared by a method patterned after that of Lespagnol.[19] The preparation of 4,4′-dichlorobenzhydryl oxalate illustrates the procedure.

4,4′-Dichlorobenzhydryl Oxalate.—A quantity of 0.536 g (4.2 mmole) of oxalic acid dihydrate was added to 25 ml of benzene, and the water was distilled as an azeotrope into a Dean-Stark trap. To the anhydrous mixture were added 1.916 g (7.6 mmoles) of 4,4′-dichlorobenzhydrol and *ca.* 10 mg of *p*-toluenesulfonic acid.[20] The mixture was heated to reflux for 12 hr, and the water produced in the reaction was removed as an azeotrope. The reaction mixture was cooled, washed twice with equal volumes of saturated sodium bicarbonate, washed twice with equal volumes of water, dried over anhydrous magnesium sulfate, and filtered. The benzene was removed on a rotary evaporator, and the crystalline residue was recrystallized from ligroin to yield 1.60 g (76%) of 4,4′-dichlorobenzhydryl oxalate, mp 142.5–143°. The infrared spectrum showed a doublet with peaks at 1775 and 1750 cm^{-1}. The nmr spectrum showed peaks at δ 7.32 (singlet, 16 H) and 6.90 (singlet, 2 H).

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.

Recrystallization of the tetrachloro oxalate from carbon tetrachloride gave beautiful crystals, mp 93–137°. Analysis of the material suggests that two molecules of carbon tetrachloride per molecule of oxalate were incorporated in the crystal since the compound analyzed for 45.96% chlorine and the bis(carbon tetrachloride) solvate should contain 49.02% chlorine.

Benzhydryl oxalate was prepared by the above method and recrystallized from carbon tetrachloride, mp 140–141° (lit.[21] mp 142–143°). The nmr spectrum showed peaks at δ 7.32 (doublet, 20 H) and 6.96 (singlet, 2 H).

Benzhydryl-α-d_1 oxalate was prepared from oxalic acid and benzhydrol-α-d_1. The crude product was recrystallized from methylene chloride and ligroin, mp 145–147°. The nmr showed no peak at δ 6.96. Mass spectral analysis showed that >95% of the oxalate contained two deuteriums.

Benzhydryl ether was prepared by the method of Ward,[22] mp 109–110° (lit.[23] mp 111°). The nmr spectra showed peaks at δ 7.30 (singlet, 20 H) and 5.40 (singlet, 2 H).

Benzhydryl diphenylacetate was prepared from benzhydrol and diphenylacetic acid by the same method used to prepare the oxalates. The crude reaction product was recrystallized from ligroin to give white crystals in 90% yield, mp 105–107° (lit.[24] mp 106°). The nmr spectrum of the ester showed a doublet at δ 7.20 (20 H), a singlet at 6.91 (1 H), and a singlet at 5.12 (1 H).

***t*-Butylperoxy diphenylacetate** was prepared by the method of Bartlett and Gortler,[16b] mp 58–60° (lit.[16b] mp 58.2–60.0°). The nmr spectrum of the perester showed singlets at δ 7.25 (10 H), 5.01 (1 H), and 1.20 (9 H).

Phenyl oxalate was synthesized by the method of Miksic and Pinterovic,[25] mp 133.5–134° (lit.[25] mp 134°).

Pyrolysis of Benzhydryl Oxalate.—Samples were placed either in a 10 × 125-mm test tube or a 50-ml, pear-shaped flask fitted with an air or water reflux condenser. Samples were flushed with nitrogen for a least 15 min before heating. For temperatures up to 235°, an electrically heated bath containing Dow Corning 550 silicone fluid was used. A Woods metal bath heated by a Tirrill burner was used for temperatures up to 350°.

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[14] (a) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1763 (1960); (b) P. D. Bartlett and R. E. Pincock, *ibid.*, **82**, 1769 (1960).

[15] Personal communication from Professor P. D. Bartlett.

[16] (a) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958); (b) P. D. Bartlett and L. B. Gortler, *ibid.*, **85**, 1864 (1963).

[17] W. S. Trahanovsky and M. P. Doyle, *J. Org. Chem.*, **32**, 146 (1967).

[18] We thank Professor G. A. Russell and Dr. E. J. Geels for the benzhydrol-α-d_1.

[19] C. Lespagnol, *Bull. Soc. Chim. France*, 110 (1960).

[20] Sulfuric acid led to a thick, intractable liquid as product.

[21] E. Linneman, *Ann.*, **133**, 23 (1865).

[22] A. M. Ward, *J. Chem. Soc.*, 2290 (1927).

[23] E. Linneman, *Ann.*, **133**, 17 (1865).

[24] H. Katagishi, Y. Ginbayashi, and M. Matsui, *Mem. Coll. Sci. Univ. Kyoto Ser. A*, **12**, 57 (1929).

[25] J. Miksic and Z. Pinterovic, *J. Prakt. Chem.*, **119**, 231 (1928).

Neat.—A quantity of 2.00 g (4.74 mmoles) of benzhydryl oxalate was pyrolyzed at 275° for 30 min. The weight lost during pyrolysis was 0.316 g which corresponds to 7.18 mmoles of carbon dioxide. The light yellow pyrolysate was separated by column chromatography on Florisil. Tetraphenylethane was eluted with pentane. Recrystallization from carbon tetrachloride gave 0.82 g (2.46 mmole) of white solid, mp 209.5–210° (lit.[26] mp 209–210°). The nmr spectrum showed a doublet at δ 7.11 (20 H) and a singlet at 4.78 (2 H). The infrared spectrum showed no carbonyl peaks. Benzhydryl diphenylacetate was eluted with 75% pentane–25% benzene. Recrystallization from ligroin gave 0.38 g (1.00 mmole) of white solid, mp 106–108° (lit.[24] mp 106°). The nmr spectrum showed peaks at δ 7.20 (doublet, 20 H) 6.93 (singlet, 1 H), and 5.13 (singlet, 1 H). The infrared spectrum showed a strong peak at 1735 cm^{-1}. The nmr and infrared spectra were identical with those of an authentic sample. Benzhydrol was eluted with 25% pentane–75% benzene. Recrystallization from ligroin gave 0.12 g (0.65 mmole) of white solid, mp 64–66° (lit.[27] mp 67–68°). The nmr spectrum showed peaks at δ 7.32 (singlet, 10 H), 5.78 (singlet, 1 H), and 2.34 (broad singlet, 1 H). The nmr and infrared spectra were identical with those of an authentic sample.

Other runs were analyzed by nmr since the products all had distinctive peaks. Diphenylmethane was added to the pyrolysate mixture, and an nmr spectrum of the mixture was taken (it was shown that diphenylmethane was not a significant product). Since no nmr peak for benzhydrol was ever detected, it must come from hydrolysis of the oxalate during chromatography. An example of this nmr method of analysis is given in the following paragraph for a run in phenyl ether solution.

Phenyl Ether Solution.—A quantity of 0.060 g (0.143 mmole) of benzhydryl oxalate in 0.555 g of phenyl ether was heated at 225° for 10 hr. After the mixture was cooled, 22.3 mg (0.133 mmole) of diphenylmethane was added to the pyrolysate. An nmr spectrum of this mixture showed peaks at δ 5.10, 4.77, and 3.94 in the ratio of 10:76:114. This gives a yield of 16% (0.023 mmole) benzhydryl diphenylacetate and 62% (0.089 mmole) of tetraphenylethane.

An equilmolar amount of tetraphenylethane and benzhydryl diphenylacetate in phenyl ether solution was heated at 225° for 24 hr under reaction conditions. Diphenylmethane was added to the mixture after heating and nmr analysis showed that 75% of the ethane and ester was still present.

Pyrolysis in the Presence of Oxygen.—Oxygen was passed through the sample before and during pyrolysis at 225° for 1 hr. Diphenylmethane was added to the product mixture and the nmr peaks at δ 7.9–7.6 (*ortho* protons of benzophenone), 5.40 (benzhydryl ether), and 3.91 (diphenylmethane) were integrated. Nmr peaks for the *ortho* protons of benzophenone could not be integrated in the case of the phenyl ether solution pyrolysate because of the large phenyl ether nmr signal.

Tetraphenylethane and benzhydryl diphenylacetate were shown to be stable under these conditions. Oxygen was passed through a mixture of 0.076 g (0.227 mmole) of tetraphenylethane and 0.0897 g (0.237 mmole) of benzhydryl diphenylacetate while it was heated at 225° for 1 hr. A quantity of 19.7 mg (0.117 mmole) of diphenylmethane was added to the cooled reaction mixture, and nmr analysis showed that at least 90% of the tetraphenylethane and benzhydryl diphenylacetate were recovered unchanged.

Pyrolysis of an Equimolar Mixture of Benzhydryl and Benzhydryl-α-d_1 Oxalate.—A mixture of 0.128 g (0.304 mmole) of benzhydryl oxalate and 0.127 g (0.300 mmole) of benzhydryl-α-d_1 oxalate in 2.404 g of phenyl ether was heated at 225° for 23 hr. The cooled pyrolysate was dissolved in 5 ml of ligroin. 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 ligroin in a similar fashion five more times. The white solid was recrystallized from ligroin, and the crystals which were tetraphenylethane were submitted to mass spectral analysis. Removal of the ligroin and phenyl ether by distillation under vacuum from the solution yielded a solid residue. The residue was recrystallized from ligroin. The crystals were largely tetraphenylethane and were separated from the mother liquor which contained the ester. Removal of the ligroin gave a solid mass which was submitted to mass spectral analysis. It was assumed that the natural isotope distribution in the oxalate-d_2 was the same as that of the oxalate-d_0. In Table III 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). From these data, the percentage of d_0, d_1, and d_2 species were calculated and presented in Table II.

TABLE III

MASS SPECTRAL DATA FOR PYROLYSATES OF NATURAL AND DEUTERATED BENZHYDRYL OXALATES

	m/e	Intensity of natural sample	Intensity of deuterated sample	Calcd peaks for d_0	Calcd peaks for d_1	Calcd peaks for d_2
		Tetraphenylethane[a]				
P	334	100	16.8	16.8	...	...
P + 1	335	29.5	36.9	5.0	31.9	...
P + 2	336	7.9	32.4	1.3	9.4	21.7
P + 3	337	...[b]	13.8	...	2.5	6.4
		Benzhydryl Diphenylacetate[c]				
P	378	100	39.7	39.7	...	...
P + 1	379	33.2	23.2	13.2	10.0	...
P + 2	380	6.9	29.0	2.7	3.3	23.0
P + 3	381	...[b]	8.2	...	0.7	7.6

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

Attempted Induced Decomposition of Benzhydryl Oxalate with Benzhydryl Radicals in Benzene Solution.—Nitrogen was bubbled for 2 min through a solution of 0.084 g (0.200 mmole) of benzhydryl oxalate and 0.057 (0.200 mmole) of *t*-butylperoxy diphenylacetate in 1.287 g of benzene. After the solution was heated under nitrogen for 2.25 hr at 70°, most of the benzene was distilled at atmospheric pressure. Nmr analysis of the residue showed that decomposition of the per 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 infrared spectrum of the residue showed the strong oxalate carbonyl doublet at 1770–1750 cm^{-1}.

Pyrolysis of 4,4′-Dichlorobenzhydryl Oxalate.—A sample of 1.860 g (2.14 mmoles) of 4,4′-dichlorobenzhydryl oxalate which contained two molecules of carbon tetrachloride per molecule of oxalate was pyrolyzed at 275° for 30 min. Yellow-orange crystals formed during the pyrolysis which were filtered before the remainder was purified by column chromatography on Florisil. The filtered crystals were recrystallized with difficulty from carbon tetrachloride and chlorobenzene to give 0.55 g (1.17 mmoles) of 4,4′,4″,4‴-tetrachloro-*sym*-tetraphenylethane, mp 358–360° dec (lit.[28] mp 350–360° dec). The infrared spectrum (KBr pellet) showed no carbonyl peak. The mass spectrum gave large molecular ion peaks at 470–474. 4,4′-Dichlorobenzhydryl 4,4′-dichlorodiphenylacetate was eluted from the Florisil column by 75% pentane–25% benzene. Recrystallization from ligroin gave 0.30 g (0.58 mmole) of fluffy, white crystals, mp 125–126° (lit.[29] mp 118). The nmr spectrum showed peaks at δ 7.18 (multiplet, 16 H), 6.82 (singlet, 1 H), and 5.04 (singlet, 1 H). The infrared spectrum showed a carbonyl absorption at 1740 cm^{-1}.

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 ligroin gave 0.10 g (0.40 mmole) of white solid, mp 90–92° (lit.[30] mp 94°). The nmr spectrum showed peaks at δ 7.24 (singlet, 8 H), 5.71 (singlet 1 H), and 2.32 (broad singlet, 1 H). The nmr and infrared spectra were identical with those of an authentic sample.

Stability of Benzhydryl Diphenylacetate.—Benzhydryl diphenylacetate was heated at 226° for 1.25 hr. Based on nmr analysis, <3% decomposition occurred.

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[26] M. L. Bert, *Compt. Rend.*, **177**, 325 (1923).

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Stability of Phenyl Oxalate.—A quantity of 83 mg of phenyl oxalate was heated at 350° for 0.5 hr. A weight loss of only 1 mg occurred, and the infrared spectrum of the reaction mixture was identical with that of starting material.

Registry No.—4,4'-Dichlorobenzhydryl oxalate, 13131-54-9; benzhydryl oxalate, 13144-28-0; benzhydryl-α-d_1 oxalate, 13144-29-1; benzhydryl ether, 575-42-5; benzhydryl diphenylacetate, 13144-31-5; *t*-butylperoxy diphenylacetate, 13144-32-6; 4,4',4'',4'''-tetrachloro-*sym*-tetraphenylethane, 13144-33-7; 4,4'-dichlorobenzhydryl 4,4'-dichlorodiphenylacetate, 13144-34-8; tetraphenylethane, 632-50-8.

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Imidazole-Catalyzed Hydrolysis of Vinyl Acetate

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Imidazole-catalyzed hydrolysis of vinyl acetate using nuclear magnetic resonance (nmr) as the monitoring technique was studied. As soon as imidazole was added to the aqueous solution of vinyl acetate, N-acetylimidazole was formed which attained a steady-state concentration in about 3 min and disappeared when the vinyl acetate was completely consumed. However, the final products of this reaction were not the expected acetaldehyde and acetic acid; instead, an addition product between the imidazole and acetaldehyde followed by acetylation was isolated whose structure is shown to be that of I by nmr, infrared, and mass spectra data. The mechanism of the formation of this product is discussed and the supporting evidence presented.

The catalytic activity of imidazole in the hydrolysis of esters is well known, especially those of substituted phenyl acetates.[2-6] Both Bruice[3] and Bender[2] proposed a mechanism for the hydrolysis of *p*-nitrophenyl acetate catalyzed by imidazole. This proposed mechanism involves a preliminary equilibrium of the imidazole and the ester to form a tetrahedral intermediate where the alkoxide ion is the preferred leaving group. The acetylated imidazole is then quickly hydrolyzed so that the net effect is an apparent imidazole-catalyzed hydrolysis as described in the text. This seems to be most probable in light of the highly labile nature of the NH hydrogen in imidazole.[7,8]

No one had investigated the imidazole-catalyzed hydrolysis of vinyl acetate. It was thought that by using nuclear magnetic resonance (nmr) to monitor the hydrolysis, it should be possible to observe and identify any long-lived intermediates formed during the course of the reaction.

Experimental Section

All the materials used are commercially available samples purified by fractional distillation. N-Acetylimidazole was prepared by the method of Reddy, Mandell, and Goldstein[8] and only freshly prepared samples were used. All the spectra were recorded on a Varian A-60 analytical spectrometer. The chemical shifts are expressed in cycles per second (cps) relative to tetramethylsilane as internal reference.

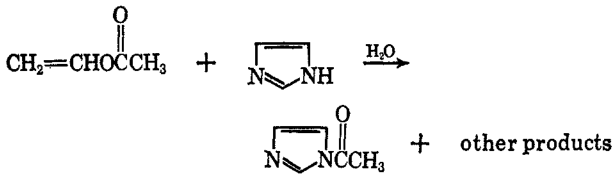
Preparation of the Final Product.—A mixture of 43 g (0.5 mole) of vinyl acetate, 34 g (0.5 mole) of imidazole, and 18 g (1 mole) of water was shaken periodically for about 2 hr. Initially, the reaction mixture became warm and was kept cool in a water bath. After 2 hr the mixture was extracted with chloroform and the extract was distilled under reduced pressure. The fraction distilling at 90° (0.6 mm) was collected. The distillate was a colorless viscous liquid. The yield was 60 g, equivalent to 80% of the theoretical yield based on the amount of imidazole taken. The nmr spectrum is given in Figure 1 and the infrared spectrum in Figure 2.

Anal. Calcd for $C_7H_{10}N_2O_2$: C, 54.50; H, 6.49; N, 18.18; O, 20.78; mol wt, 154. Found: C, 54.00; H, 6.47; N, 18.90; O, 20.63; mol wt, 154 (by mass spectrometry).

A small amount of imidazole was found to be present in the distillate which can account for the slightly higher value for nitrogen and lower value for oxygen found in the elemental analysis.

Results and Discussion

An aqueous solution (5–10% by volume) of vinyl acetate gave the same nmr spectrum as the solution in usual organic solvents indicating that no reaction took place within a reasonable length of time. The methyl group resonance of vinyl acetate was at −124 cps relative to tetramethylsilane. When imidazole was added to this solution and the spectrum recorded immediately, an additional methyl group resonance was observed. The frequency of this peak is at −151 cps and corresponded to the acetyl methyl group resonance of N-acetylimidazole.[8] The intensity of the new peak increased to a maximum in about 3 min and remained constant until most of the vinyl acetate reacted. Simultaneously, additional peaks were observed in the general region of the ring protons of imidazole and corresponded to the three protons of N-acetylimidazole.[8] This clearly suggested that the first and relatively fast step in this reaction is the formation of N-acetylimidazole from the reaction of vinyl acetate with imidazole.



During the initial periods of the reaction, no spectra belonging to either vinyl alcohol or acetaldehyde were

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