The high negative entropy of activation (−28 eu) as determined from the rate constants for method A is believed to be due to both the entropy of activation for the removal of a proton from the 2-methyl group of N-acetoxy-2-methylquinolinium ion and to the entropy for the reaction which results in the formation of N-acetoxy-2-methylquinolinium acetate. Separation of these entropy factors will be necessary before their individual evaluation can be made.

Registry No.—**1**, 1076-28-4; acetic anhydride, 108-24-7; α,α,α-trideuterio-2-methylquinoline 1-oxide, 16649-54-0; N-acetoxy-2-methylquinolinium perchlorate, 1658-39-5; tetra-*n*-butylammonium acetate, 10534-59-5; hexadeuterioacetic anhydride, 16649-49-3.

Acknowledgments.—The authors are indebted to Dr. George A. Hall, Jr., Dr. C. Gordon McCarty, and Dr. Vincent J. Traynelis for valuable discussions during this investigation. We thank Miss Evie Pakas, who, as a 1967 National Science Foundation Summer Research Participant, carried out the rate studies involving nmr spectroscopy. We also acknowledge with pleasure the technical assistance which Mr. Robert Smith gave us in connection with the nmr studies and to Mr. David Chapman for his assistance with the computer programming.

Lead Tetraacetate Oxidation of 4,4,4-Triphenyl-1-butanol, 3,3,3-Triphenyl-1-propanol, and 4,4,4-Triphenylbutyric Acid

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Received February 26, 1968

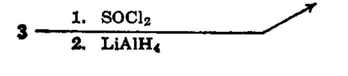
Lead tetraacetate oxidations of 4,4,4-triphenyl-1-butanol (**1**), 3,3,3-triphenyl-1-propanol (**2**), and 4,4,4-triphenylbutyric acid (**3**) were carried out in benzene solution at 70°. In the absence of oxygen the major products obtained from **1** were 1,1-diphenylindan (**8**), 2,3,4,5-tetrahydro-5,5-diphenyl-1-benzoxepin (**9**), and 4,4,4-triphenyl-1-butyl acetate (**4**); from **2**, 4,4-diphenylchroman (**18**) and 3,3,3-triphenyl-1-propyl acetate (**5**); and from **3**, indan **8** exclusively. In the presence of oxygen little (if any) **8** was formed from alcohol **1** or acid **3**, and in both of these cases the cyclic ether, **18**, was shown to be a major product. On the basis of these results and other supporting evidence, it is argued that 3,3,3-triphenylpropyl radical (**19**) is a prime intermediate in the lead tetraacetate oxidations of **1** and **3**, that anchimeric assistance due to phenyl participation is not involved in the oxidative deformylation of **1** or in the oxidative decarboxylation of **3**, and that relief of steric compression provides a driving force for the unexpectedly facile deformylation of **1**. The data are shown to be consistent with a radical chain mechanism previously proposed for the lead tetraacetate oxidation of monohydric alcohols. Possible reasons are considered for the apparent absence of carbon–oxygen phenyl migration in the lead tetraacetate oxidations of **1**–**3**, and independent methods of synthesis for several of the possible oxidation products (including the novel cyclic ether, **9**) are described.

Because of its unusually high tendency to undergo homolytic rearrangement, the trityl function has received extensive study as a neighboring group[1] in homolytic and quasihomolytic reactions.[2] We previously demonstrated the occurrence of trityl group rearrangements in the lead tetraacetate oxidations of 3,3,3-triarylpropionic acids[2s] and triarylmethanols[2t] and performed quantitative migratory aptitude measurements on these reactions. On the basis of results obtained with the latter system, a chain sequence involving the successive formation of alkoxy radicals, carbon radicals, and carbonium ions (either actual or incipient) was proposed as a general mechanism for the oxidation of most types of monohydric aliphatic alcohols with lead tetraacetate.[2t] In a continuation of our studies of the properties of trityl as a neighboring group in lead tetraacetate oxidations, we now report work dealing with the oxidation of alcohols **1** and **2** and the acid **3**. These oxidations, particularly that of **1**, exhibit certain unusual features that are not predictable from the results of previous studies on related systems. Most significantly, this work has provided additional strong evidence for the involvement of radicals in the lead tetraacetate oxidation of monohydric alcohols.

$Ph_3C(CH_2)_nX$
1, $n = 3$; $X = OH$
2, $n = 2$; $X = OH$
3, $n = 2$; $X = CO_2H$
4, $n = 3$; $X = OAc$
5, $n = 2$; $X = OAc$
6, $n = 2$; $X = CHO$

Results and Discussion

Oxidation of 4,4,4-Triphenyl-1-butanol (1).—Alcohol **1** was synthesized in two ways. The preferred method involved hydroboration–oxidation of the olefin, **7**,



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[1] As used here, the term "neighboring group" does not necessarily imply the involvement of anchimeric assistance in bond-breaking processes.

[2] For representative examples, see (a) H. Wieland, *Ber.*, **44**, 2550 (1911); (b) M. A. Spielman, *J. Amer. Chem. Soc.*, **57**, 1117 (1935); (c) M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **15**, 763 (1950); (d) M. S. Kharasch, A. C. Poshkus, A. Fono, and W. Nudenberg, *ibid.*, **16**, 1458 (1951); (e) P. D. Bartlett and J. D. Cotman, Jr., *J. Amer. Chem. Soc.*, **72**, 3095 (1950); (f) R. M. McNeer, Ph.D. Thesis, University of Chicago, 1953; (g) S. J. Cristol and J. E. Leffler, *J. Amer. Chem. Soc.*, **76**, 4468 (1954); (h) D. Y. Curtin and T. C. Miller, *J. Org. Chem.*, **25**, 885 (1960), and earlier papers by Curtin, *et al.;* (i) L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 4531 (1966); (j) D. B. Denney and N. F. Newman, *ibid.*, **89**, 4692 (1967); (k) H. Breederveld and E. C. Kooyman, *Rec. Trav. Chim.*, **76**, 297 (1957); (l) J. W. Wilt and D. D. Oathoudt, *J. Org. Chem.*, **23**, 218 (1958); (m) J. W. Wilt and J. L. Finnerty, *ibid.*, **26**, 2173 (1961); (n) J. W. Wilt and J. A. Lundquist, *ibid.*, **29**, 921 (1964); (o) W. Rickatson and T. S. Stevens, *J. Chem. Soc.*, 3960 (1963); (p) D. B. Denney, R. L. Ellsworth, and D. Z. Denney, *J. Amer. Chem. Soc.*, **86**, 1116 (1964); (q) C. Rüchardt and R. Hecht, *Ber.*, **98**, 2460 (1965); (r) W. H. Starnes, Jr., *J. Amer. Chem. Soc.*, **85**, 3708 (1963); (s) W. H. Starnes, Jr., *ibid.*, **86**, 5603 (1964); (t) W. H. Starnes, Jr., *ibid.*, **89**, 3368 (1967), and **90**, 1807 (1968).

TABLE I

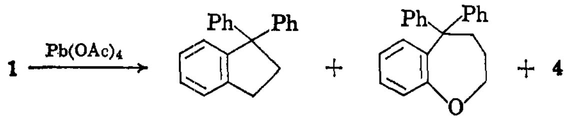
LEAD TETRAACETATE OXIDATIONS[a]

		Yield,[b] %									
Expt	Compd	**1**	**2**	**3**	**4**	**5**	**6**	**8**	**9**	**18**	**21**
1[c]	1	20 ± 1	...	...	35 ± 2	...	*d*	5 ± 1	9 ± 2	...	...
2[e]	1	19 ± 7	...	7 ± 5	14 ± 2	...	...	<1[f]	16 ± 2	11 ± 1	...
3	2	...	14	...	...	39	...	...	...	24	<1
4[g]	3	...	...	78	...	...	...	8	...	...	...
5[e,g]	3	...	...	82	...	...	...	<1[f]	...	1	...

[a] 1.62 mmol of compd, 3.25 mmol of $Pb(OAc)_4$, 5.0 mmol of $CaCO_3$, 15 ml of benzene, 70 ± 1°, 21.0 hr, He atmosphere. [b] Deviations refer to duplicate runs. [c] Ethylene yield, 1.5%; identification tentative. [d] Trace detected by nmr spectroscopy. [e] Run under O_2 atmosphere. [f] Identification uncertain. [g] Reaction time, 95.0 hr.

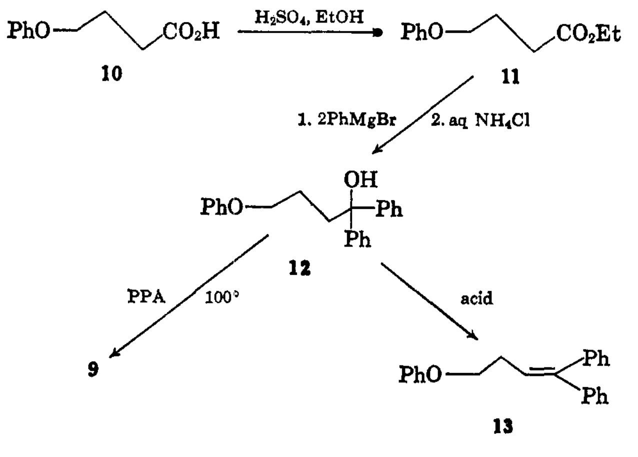
which is easily obtained from trityl and allyl chlorides in a Grignard coupling reaction.[3] An alternative procedure involving lithium aluminum hydride reduction of the acyl chloride corresponding to acid **3** also gave good results but was considerably less convenient owing to the rather lengthy sequence of reactions required for the preparation of **3** according to a published method.[2a]

Oxidation of **1** with 2 mol of lead tetraacetate in an oxygen-free atmosphere (expt 1, Table I) gave as principal products 1,1-diphenylindan (**8**), 2,3,4,5-tetrahydro-5,5-diphenyl-1-benzoxepin (**9**), and the acetate (**4**) of the starting alcohol, together with appreciable amounts of unchanged **1** and some minor products. Structures of the three major products were confirmed by comparing their properties with those of authentic, independently synthesized specimens. The previously unreported acetate, **4**, was easily secured by acetylation of **1** with acetic anhydride, while **8** was readily obtained from 3,3-diphenyl-1-indanone by Wolff–Kishner reduction (Huang-Minlon modification). Ether **9**, a novel representative of a relatively rare ring system, was prepared by a sequence starting with 4-phenoxybutyric acid (**10**) and proceeding *via* ester **11** and alcohol **12** in the manner depicted in Scheme I. Closure of the seven-membered ring occurred to the extent of 30% when the heterogeneous reaction of **12** and polyphosphoric acid (PPA) was carried out with very efficient stirring. When performed with inefficient stirring, this reaction gave excellent yields of the new olefin, **13**, a product which was also recovered in high yields after exposure of **12** to the action of certain other acidic reagents (see Experimental Section).



8 **9**

SCHEME I



A possible outcome of the lead tetraacetate oxidation of **1** is stepwise or concerted decomposition of the alcohol into three stable fragments: trityl radical (or cation), ethylene, and formaldehyde. Indeed, the probable formation of ethylene in expt 1 suggests that this type of process did occur to some extent. However, the very low yield of ethylene and the absence of appreciable amounts of trityl acetate (or its hydrolysis product, tritanol) indicate that multiple fragmentation was a minor reaction path, at most.

Formation of **8** in the lead tetraacetate oxidation of **1** was quite unexpected, since no β-scission products had previously been obtained from lead tetraacetate oxidations of other primary aliphatic alcohols having the general structure RCH_2CH_2OH (R = alkyl or substituted alkyl),[4] even in cases where competing processes leading to saturated cyclic ethers were strongly disfavored by structural factors (*e.g.*, 1-propanol,[4b,i] 4,4-dimethyl-1-pentanol,[4d] 4,4-dimethyl-1-hexanol[4d]). Consideration was given to the possibility that deformylation of **1** was facilitated by a release of steric compression on going from the ground state to the transition state for cleavage, but this explanation seemed unlikely *a priori* in view of the rather large distance between the trityl group and the reaction site, the absence of cleavage in the oxidation of alcohols having similar structures (4,4-dimethyl-1-pentanol,[4d] 4,4-dimethyl-1-hexanol[4d]), and the general lack of evidence for steric acceleration of alkoxy radical fragmentations.[5] On the other hand, the possible occurrence of a concerted deformylation process leading directly to **14** (radical or cation) *via* a cyclic transition state such as **15** or **16** (either homolytic or heterolytic in the case of **15**) was suggested by the structure of the deformylation product (**8**) and by the known formation of major amounts of cleavage products in lead tetraacetate oxidations of other primary alcohols capable of yielding resonance-

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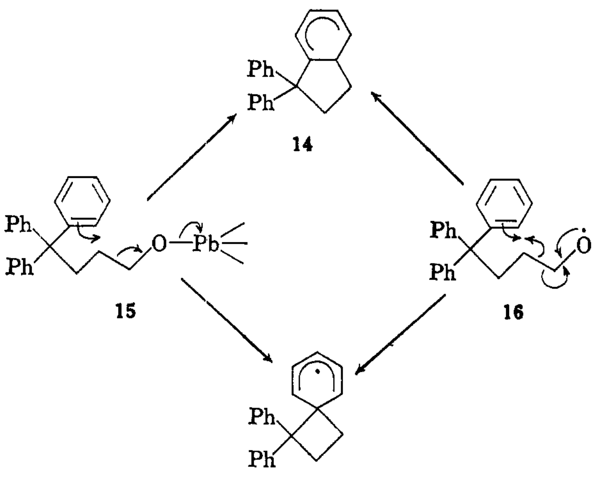
(3) A. N. Nesmeyanov and E. G. Perevalova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1002 (1954); *Chem. Abstr.*, **49**, 6892 (1955).

(4) (a) V. M. Mićović, R. I. Mamuzić, D. Jeremić, and M. L. Mihailović, *Tetrahedron*, **20**, 2279 (1964); (b) M. L. Mihailović, Z. Maksimović, D. Jeremić, Ž. Čeković, A. Milovanović, and L. Lorenc, *ibid.*, **21**, 1395 (1965); (c) M. L. Mihailović, Ž. Čeković, Z. Maksimović, D. Jeremić, L. Lorenc, and R. I. Mamuzić, *ibid.*, **21**, 2799 (1965); (d) M. L. Mihailović, Ž. Čeković, and D. Jeremić, *ibid.*, **21**, 2813 (1965); (e) M. L. Mihailović, J. Bošnjak, Z. Maksimović, Ž. Čeković, and L. Lorenc, *ibid.*, **22**, 955 (1966); (f) M. L. Mihailović and M. Miloradović, *ibid.*, **22**, 723 (1966); (g) M. L. Mihailović, L. Živković, Z. Maksimović, D. Jeremić, Ž. Čeković, and R. Matić, *ibid.*, **23**, 3095 (1967); (h) D. Hauser, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **47**, 1883 (1964); (i) R. E. Partch, *J. Org. Chem.*, **30**, 2498 (1965); (j) S. Moon and P. R. Clifford, *ibid.*, **32**, 4017 (1967).

(5) J. D. Bacha and J. K. Kochi, *J. Org. Chem.*, **30**, 3272 (1965); F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N. Smith, and P. M. Zanet, *ibid.*, **28**, 55 (1963).

SCHEME II



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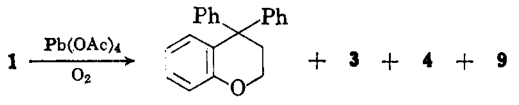
stabilized cleavage fragments (benzyl[4g,6] or allyl[6]) (see Scheme II).

In an attempt to decide among these various mechanistic possibilities, the lead tetraacetate oxidation of **1** was repeated under an atmosphere of pure oxygen (expt 2, Table I). Under these conditions little (if any) **8** was formed, and a new cleavage product, 4,4-diphenylchroman (**18**), was produced, together with acid **3** (presumably arising *via* autoxidation of aldehyde **6**) and the other anticipated products.



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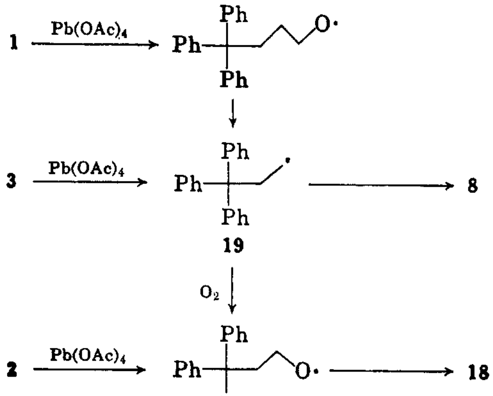
SCHEME III



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Compound **18** is undoubtedly formed by a mechanism involving entrapment of 3,3,3-triphenylpropyl radical (**19**) by molecular oxygen. The peroxy radical produced in this way could be converted into a number of possible intermediates capable of yielding **18** directly; however, we prefer to formulate the cyclizing intermediate as the alkoxy radical, **20** (see Scheme III).[7] The formation of **18**, coupled with the essentially complete absence of **8** from the products of expt 2, strongly suggests that radical **19** (or the cation resulting from its subsequent oxidation)[8] is also the precursor of **8** and militates against formation of **8** *via* the concerted processes considered above. Consideration must also be given, of course, to the possibility that a concerted process leading directly to **14** is followed by a rapid conversion of this species to radical **19**. However, **14** must be more stable than **19** if formation of **14** is to provide a driving force for deformylation. Conversion of **14** into **19** would then have to be an endothermic process requiring a significant energy of activation.[9] This type of process would not be expected to compete effectively with relatively rapid reactions such as the oxidation of **14** by Pb^{IV} or oxygen.[10] A similar argument can be made against alternative concerted mechanisms involving the direct production of radical **17**. It should also be noted that formation of **17** would require an energetically unfavorable four-membered cyclic transition state, and that this radical would be expected to yield appreciable amounts of product(s) resulting from phenyl migration, which could occur either before or after rapid radical oxidation.

If the foregoing arguments are accepted, one is forced to conclude that the driving force for oxidative deformylation of **1** is provided by rather subtle structural factors. Unlikely though it appeared at the outset, we now suspect that release of ground-state compression is, in fact, the correct explanation. The basis for this supposition is provided by certain unusual features appearing in the 100-MHz nmr spectra of compounds **1–6** and several related substances currently under study in this laboratory. In all of these cases we have found that the protons of the methylene group α to the trityl function exhibit complex splitting patterns due to magnetic nonequivalence. Similar behavior is observed with the β-methylene protons, and comparisons of the spectra of homologous pairs of compounds show that deviations from first-order splitting are more pronounced when $n = 3$ rather than 2 (see general structure for **1–6**). When $n = 1$, the methylene protons

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[6] S. Moon and J. M. Lodge, *J. Org. Chem.*, **29**, 3453 (1964).

[7] (a) Possible reactions leading to the alkoxy radical are $2RO_2\cdot \rightarrow 2RO\cdot + O_2$; and $RO_2\cdot + \text{H donor} \rightarrow RO_2H$, followed by $RO_2H \rightarrow RO\cdot + HO\cdot$. Any ROH formed by H abstraction might be reconverted into RO· by reaction with Pb(IV); a similar reconversion of RO_2H into $RO_2\cdot$ also seems possible [*cf.* P. D. Bartlett and P. Günther, *J. Amer. Chem. Soc.*, **88**, 3288 (1966)]. However, extensive formation of alcohol **2** seems unlikely, since this should have led to the production of an appreciable amount of acetate **5** (see expt 3, Table I). Direct (concerted) cyclization of RO_2H has no well-established analogies. (b) Direct cyclization of a Pb(IV) alcoholate is disfavored by the lack of evidence for neighboring phenyl participation in the lead tetraacetate oxidation of triphenylmethanol.[2t] Intramolecular addition followed by radical oxidation is clearly the preferred route from RO· to ethers such as **9** and **18**. An alternative sequence involving H abstraction, aryl radical oxidation, and internal solvation seems highly unlikely in view of the high strengths of aryl C–H bonds [J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966)] and the high energy of the phenyl cation [I. P. Fisher, T. F. Palmer, and F. P. Lossing, *J. Amer. Chem. Soc.*, **86**, 2741 (1964)]. For another argument against the latter type of mechanism, see ref 4g.

[8] (a) Both intermediates could be involved, since the oxidation of primary alkyl radicals by Pb(IV) is relatively slow: (b) J. K. Kochi, *J. Amer. Chem. Soc.*, **87**, 3609 (1965); (c) J. K. Kochi, J. D. Bacha, and T. W. Bethea, III, *ibid.*, **89**, 6538 (1967); (d) J. D. Bacha and J. K. Kochi, *J. Org. Chem.*, **33**, 83 (1968).

[9] Reversible addition of simple primary aliphatic radicals to aromatic nuclei has apparently never been observed. In this connection it also seems pertinent to note that the additions of trifluoromethyl or chlorodifluoromethyl radicals to benzene have been shown to be essentially irreversible in the vapor phase at temperatures below 100° [G. E. Owen, Jr., J. M. Pearson, and M. Szwarc, *Trans. Faraday Soc.*, **61**, 1722 (1965); J. R. Majer, D. Phillips, and J. C. Robb, *ibid.*, **61**, 110 (1965)].

[10] Although rate constants are not available for the oxidation of cyclohexadienyl-type radicals by Pb(IV), the structural correlations of Kochi[8b–d] suggest that these oxidations are probably faster than the rapid competing processes of dimerization and disproportionation. For examples and a discussion of the rapid oxidation of cyclohexadienyl-type radicals with oxygen, see D. H. Hey, "Advances in Free-Radical Chemistry," Vol. II, G. H. Williams, Ed., Logos Press Ltd., London, England, p 65 ff.

appear as a sharp singlet. Although a complete explanation of these observations is lacking, they clearly suggest the presence of rotational restrictions (steric compressions) which become less pronounced as the length of the alkyl chain is decreased. We hope that a fuller analysis of these spectra[11] will lead to a rigorous explanation of the observed nonequivalences and permit a firm decision regarding their possible connection with the relatively facile deformylation of **1**.

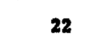
Oxidation of 3,3,3-Triphenyl-1-propanol (**2**).—Lead tetraacetate oxidation of alcohol **2** gave results that were consistent with the mechanistic scheme presented in Scheme III. The identified products of this reaction (expt 3, Table I) were cyclic ether **18** (isolated in a preparative run and shown to be identical with the product from expt 2), acetate **5**, unchanged starting alcohol, and a trace of 3,3,3-triphenylpropionic acid, **21** (probably formed by autoxidation of the corresponding aldehyde during work-up). Here again we prefer to formulate the cyclizing species as radical **20**, although direct cyclization of a Pb^{IV} alcoholate is not completely ruled out.[7b]

Oxidation of 4,4,4-Triphenylbutyric Acid (**3**).—Lead tetraacetate oxidations of acid **3** were carried out under conditions strictly analogous to those used with alcohols **1** and **2**. In the absence of oxygen (expt 4, Table I) **3** reacted very slowly to give the indan, **8**. In the presence of oxygen (expt 5, Table I) the extent of conversion of the acid was even less, and the only identifiable product of the reaction was the ether, **18**. These results, summarized in Scheme III, are consistent with previous observations in support of a radical chain mechanism for the oxidative decarboxylation of primary aliphatic acids with lead tetraacetate,[8b,d] and they provide strong evidence for the presence of a common intermediate, radical **19**, in the oxidations of **1** and **3**. In accordance with the arguments presented above regarding the mechanism of deformylation of **1**, we therefore conclude that the oxidative decarboxylation of **3** is not anchimerically assisted by phenyl participation. Also consistent with this conclusion is the very slow rate of reaction of **3**, since in this respect **3** behaves like the primary aliphatic acids studied by Kochi under similar conditions.[8b]

Rearrangements and Cyclizations Involving the Trityl Group.—A further point of interest concerning the oxidation of acid **3** is the apparent absence of products (phenyl esters) resulting from intramolecular migration of a phenyl group to carboxyl oxygen. In this respect the oxidation resembles the Hunsdiecker reaction of **3** and the thermal decomposition of the corresponding diacyl peroxide.[2n] On the other hand, carbon–oxygen phenyl migration is a major process in the lead tetraacetate oxidation of acid **21** and in other reactions which are potential sources of radical **22**.[2k–s] The reason for the different rearrangement tendencies of radicals **22** and **23** (or structurally related intermediates) is a rather intriguing question,[2n] and in the case of the anomalous Hunsdiecker reaction of acid **21** it has been suggested that development of the highly conjugated system of the rearrangement product, phenyl 3,3-diphenylacrylate, may provide a driving force for phenyl migration.[2n] However, this explanation requires that the aryl shift proceed entirely *via* an extraordinary bimolecular mechanism involving abstraction of methylene hydrogen in a preliminary step or in the slow step of the rearrangement, and it does not account for the formation of phenyl 3,3-diphenylpropionate upon thermal decomposition of the *t*-butyl perester of acid **21**.[2r] Denney, *et al.*,[2p] have discussed the possible effects of conformation, decarboxylation rate, and other factors on the facile rearrangement of radical **22**. The present work leads to one further suggestion regarding the problem in question, namely, that the conformational changes required to reach a cyclic transition state are more extensive in the case of **23** and may be subject to a steric retardation (see above) which is absent or attenuated in the case of the smaller radical (**22**).

$Ph_3CH_2CO_2H$

21



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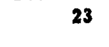

23

$Ph_2\dot{C}(CH_2)_nOPh$

24a, $n = 2$

b, $n = 3$

In view of the facile 1,4-phenyl migration observed with **22** and its potential precursors, the complete absence of 1,4-rearrangement products from the lead tetraacetate oxidation of alcohol **2** is quite surprising. We have no convincing explanation for this result and can only suggest that perhaps the branched structure of the carboxyl group exerts a special conformational bias in favor of the five-membered cyclic transition state[2k,m,r,s] responsible for rearrangement and allows the process to occur with a minimal loss of rotational entropy. Since the ring formed from **2** is actually six membered, one might expect the occurrence of 1,5-phenyl migration *via* a cyclic six-membered transition state in the lead tetraacetate oxidation of alcohol **1**, but this prediction also seems to be contradicted by experiment. However, interpretation of these results is complicated by the possibility that the cyclic ethers, **9** and **18**, are actually formed in a *two-stage* process which includes phenyl migration as the *initial step*. Cyclization of the rearranged radicals formed in this way (**24a** and **b** or the analogous cations produced by subsequent oxidation) could lead to the observed products, if only in theory.[12] This type of mechanism cannot be ruled out completely, though it does seem unlikely in view of the apparent absence of noncyclized products (phenyl ethers) derived from radicals **24a** and **b**. Moreover, formation of six-membered cyclic ethers (chroman[4g,j] and 1,4-benzodioxan[4f]) in the lead tetraacetate oxidations of other phenyl-substituted alcohols whose structures supply no strong driving force for rearrangement suggests that phenyl migration is not involved in the oxidation of alcohol **2**, at least.[7b]

Mechanism of the Lead Tetraacetate Oxidation of Monohydric Alcohols.—The demonstrated presence of radical **19** in the lead tetraacetate oxidation of alcohol **1** constitutes conclusive evidence for a homolytic *β*-scission process and is consistent with the general mechanism previously proposed for such oxidations.[2t] This

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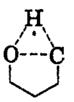
[11] Work with Dr. J. J. R. Reed of this laboratory is currently in progress. It is interesting to note that similar magnetic nonequivalences are also observed with alcohol **12** (see Experimental Section).

[12] In principle, *all* intramolecular cyclizations involving the trityl group can be accounted for in terms of similar two-stage mechanisms.

result also provides good indirect evidence for operation of a radical chain mechanism in the Pb^{IV} oxidation of alcohols to saturated cyclic ethers, since previous studies have strongly suggested that this mode of reaction and the β-scission process are mechanistically similar.[4e,13] In these systems the presence of efficient radical scavengers should decrease the yields of products formed *via* the general chain mechanism and increase the yields of products (*e.g.*, acetates of starting alcohols[14]) formed by competing nonradical processes. However, Table I shows that the lead tetraacetate oxidation of alcohol **1** gives increased yields of cyclized products and a lower yield of acetate **4** when oxygen is added to the system. This result suggests that short kinetic chains are involved in the formation of the cyclized materials, and that the rate of chain initiation is faster when oxygen is present. The latter effect may be connected with the formation of oxidation products such as water and methanol (from oxygen and methyl radicals). Coordination or metathetical reactions of these products with a Pb^{IV} alcoholate of **1** might have produced new Pb^{IV} species capable of undergoing more rapid homolysis. Under these conditions it is also possible that partial hydrolysis or methanolysis of the product acetate (**4**) occurred, making more of the starting alcohol available for reaction by the homolytic path.

The possible intervention of a bridged radical species, **25**, has been considered in connection with the lead tetraacetate oxidation of monohydric alcohols.[15]



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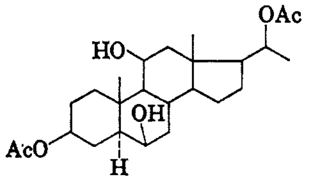

26

It has been suggested that, in sterically constrained systems, tetrahydrofuran formation may occur *via* direct oxidation of **25**, rather than by a more conventional mechanism involving intramolecular hydrogen abstraction by an alkoxy radical, followed by oxidation of the resulting carbon radical to a carbonium ion (or ion pair).[15] Thus, the fact that lead tetraacetate oxidation of the 6β,11β-dihydroxy steroid, **26**, gives 6β,19-oxide exclusively, even though the two hydroxyl groups are equidistant from C-19, is said to rule out the presence of an ion-pair intermediate.[15] However, this argument fails to consider the possibility that steric interaction of the counteranion with the axial hydrogen at C-4 might have kept an intimate ion pair from attaining the optimum conformation needed for internal solvation by the 11β-hydroxyl.[16] Oxidation of steroidal alcohols by the "hypoiodite" method (photolysis in the presence of lead tetraacetate and iodine) occasionally yields products that appear to have been formed from carbonium ion intermediates. These products sometimes differ from those obtained upon oxidation of the same alcohols with lead tetraacetate alone, and in certain instances the differences have been used to make a case against carbonium ions in the lead tetraacetate reaction.[15,17] This type of argument also seems tenuous at best, since the detailed mechanism of the "hypoiodite" reaction has not been established, and since the partitioning of ion-pair intermediates among competing reaction paths might be influenced to a considerable degree by the nature of the counteranions, which could easily be different for the two reactions in question. In view of these considerations, we conclude that the involvement of a transition state or intermediate symbolized by **25** requires further experimental verification.

Experimental Section[18]

Materials.—Lead tetraacetate (Matheson) was dried in a vacuum desiccator containing sodium hydroxide. Anhydrous calcium carbonate (Matheson, A.C.S. reagent) was stored in a vacuum oven at 60° under 5–10-mm pressure. Benzene (Baker reagent) was dried over sodium ribbon. All other chemicals used were either highly purified commercial products or compounds prepared in this laboratory by the indicated literature procedures. Purities were verified by spectral measurements, determinations of appropriate physical constants, and, where possible, by vpc analysis.

4,4,4-Triphenylbutyric Acid (3).—Acid hydrolysis of 4,4,4-triphenylbutyronitrile[2n] according to a published procedure,[2n] followed by recrystallization of the crude product from aqueous ethanol, gave **3** in 90% yield: mp 155–157° (lit.[2n] mp 159–160°); ir (CS_2) 1704 (strong, carboxyl C=O, lit.[2n] for **3**, 1712) and 2550–2700 cm^{-1} (broad and weak, carboxyl OH); nmr (CCl_4), δ 11.62 (broad s, 1, CO_2H), 7.0–7.3 (m, 15, three C_6H_5), 2.75–3.03 (m resembling t, 2, Ph_3CCH_2), and 1.95–2.23 ppm (m resembling t, 2, CH_2CO_2H).

4,4,4-Triphenyl-1-butanol (1). A. From 4,4,4-Triphenylbutyric Acid (3).—Acid **3** (3.00 g, 9.48 mmol) was stirred under reflux with thionyl chloride (10 ml) for 2.3 hr. Evaporation of the mixture gave a residue which was freed of excess reagent by repeated dissolution in benzene followed by reevaporation. The solid thus obtained (mp 87–89°, presumably the acyl chloride) was taken up in dry ether (50 ml), and the solution was stirred under nitrogen while a large excess of lithium aluminum hydride (0.72 g, 19 mmol) in dry ether (20 ml) was added dropwise during 10 min. After 1.7 hr of refluxing, followed by cautious treatment with excess water and 10% hydrochloric acid, the ether layer was separated, washed with 1 *N* sodium carbonate solution, dried, and evaporated to give 2.75 g (96%) of alcohol **1**, mp 120–122°. Two recrystallizations from cyclohexane gave slender, snow-white needles: mp 122–123°; ir (CS_2) 3584 cm^{-1} (medium, OH), no carbonyl absorption; nmr (CCl_4, 60°), δ 6.9–7.3 (m, 15, three C_6H_5), 3.48 (t, 2, J = 6 Hz, CH_2OH), 2.53–2.70 (m, 2, Ph_3CCH_2), 1.13–1.44 (m, 2, CH_2CH_2OH), and 1.04 ppm (s, 1, OH); mass spectrum (70 eV) *m/e* 302.1670 (weak; calcd for $C_{22}H_{22}O$, 302.1670), 284.1557 (medium; calcd for $C_{22}H_{20}$, 284.1565), and 243.1185 (strong; calcd for $C_{19}H_{15}$, 243.1174).

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[15] K. Heusler and J. Kalvoda, *Angew. Chem. Intern. Ed. Engl.*, **3**, 525 (1964).

[16] *Cf.* the discussion of the structures of intimate ion pairs by S. Winstein and G. C. Robinson, *J. Amer. Chem. Soc.*, **80**, 169 (1958).

[17] D. Hauser, K. Heusler, J. Kalvoda, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **47**, 1961 (1964).

[18] Boiling points and melting points are uncorrected. The melting points were determined with a Fisher-Johns apparatus. Elemental microanalyses were done by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., or by Galbraith Laboratories, Inc., Knoxville, Tenn. Evaporations were carried out at ambient temperature under 5–10 mm pressure on rotary evaporators. Infrared, 100-MHz nmr, and high resolution mass spectra were obtained with a Perkin-Elmer instrument (Model 21), a Varian Associates instrument (Model HA-100), and an AEI MS-9 spectrometer, respectively. Unless noted otherwise, nmr measurements were made at room temperature using dilute solutions that contained TMS for internal standardization. Nmr peak multiplicities are abbreviated as follows: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), qr (quartet), qn (quintet), and m (multiplet). Exact mass measurements are referred to C = 12 μ. Programmed temperature vpc analyses were done with an F & M instrument (Model 500) equipped with a 6 ft × 0.25 in. (o.d.) stainless steel column containing SE-30 (15%) on 45–60 mesh Chromosorb W. The carrier gas was helium; column temperature was increased from 100 to 350° at the rate of 8°/min. Various instrumental analyses were performed by Miss T. Reid and Messrs. B. R. Coltharp, T. J. Denson, J. Dzilsky, T. Hines, H. W. Kinsey, R. J. LeCompte, G. C. McCollum, A. C. Raymer, V. H. Rushing, G. R. Taylor, and J. L. Taylor.

Anal. Calcd for $C_{22}H_{22}O$: C, 87.37; H, 7.33. Found: C, 87.68; H, 7.42.

A compound that melted at 240° and was assigned the structure of 1 has been reported to result from reaction of trityl Grignard reagent with trimethylene oxide.[19] In the present work no attempts were made to resolve this discrepancy, since the structure of our sample of 1 was conclusively established by the foregoing observations and by the following independent synthesis.

B. From 4,4,4-Triphenyl-1-butene (7).—A solution of the olefin[3] (15.38 g, 54.1 mmol) and sodium borohydride (0.784 g, 20.7 mmol) in 40 ml of purified, anhydrous diglyme was prepared in a dry apparatus under nitrogen (inert atmosphere was maintained during entire reaction period) and stirred at 24–25° (water bath cooling) while a solution of concentrated sulfuric acid (0.581 ml, 10.4 mmol) in dry ether (14 ml) was added dropwise during 10 min. After 3.5 hr of stirring at ambient temperature and 1.5 hr at 70–75°, the mixture was cooled to 32°, treated rapidly in succession with 1.5 ml of water and 6.8 ml of 3 *N* sodium hydroxide, and kept at 33–35° by means of an ice-water bath while 6.8 ml of 30% aqueous hydrogen peroxide was introduced during 15 min with continued stirring. The cooled mixture was stirred at 27–33° for 20 min; then the cooling bath was removed; and stirring was continued for an additional 6.5 hr at ambient temperature. Removal of the product was accomplished by extraction with three 30-ml portions of ether; and, after dilution with a large additional quantity of ether in order to prevent precipitation of the alcohol during subsequent operations, the combined extracts were washed five times with ice water, dried, and evaporated. Recrystallization of the solid residue from cyclohexane afforded 10.58 g of alcohol 1, mp 120–121°; a second crop weighing 0.81 g (total yield, 70%) and, melting at 118–120° was also recovered. A further recrystallization from cyclohexane gave a product that melted at 122–123° and was identical in every respect [vpc, ir, mass spectrometry (ms), nmr] with a sample of 1 prepared according to procedure A, above.

3,3,3-Triphenyl-1-propanol (2).—Wilt and Lundquist[2n] described the preparation of this alcohol from 3,3,3-triphenylpropionic acid *via* lithium aluminum hydride reduction of the corresponding acyl chloride. Their method was employed in the present work, using a detailed procedure analogous to method A for alcohol 1. From 42.7 g (0.141 mol) of the acid and 100 ml of thionyl chloride there was obtained 45.1 g of crude acyl chloride; this afforded 39.7 g (98%) of 2 upon reduction with 10.70 g (0.282 mol) of lithium aluminum hydride. The crude alcohol was actually quite pure: it melted at 108.5–110° (lit.[2n] mp 107.5–108°) and showed no change in melting point after recrystallization from cyclohexane; ir (CS_2) 3610 cm^{-1} (medium, OH), no carbonyl absorption; nmr (CCl_4), δ 6.91–7.24 (m, 15, three C_6H_5), 3.29 (distorted t, 2, $J \approx 7$ Hz, CH_2OH), 2.77 (distorted t, 2, $J \approx$ Hz, Ph_3CCH_2), and 2.18 ppm (s, 1, OH); mass spectrum (70 eV) m/e 288.1522 (weak; calcd for $C_{21}H_{20}O$, 288.1514), 270.1406 (medium; calcd for $C_{21}H_{18}$, 270.1408), and 243.1174 (strong; calcd for $C_{19}H_{15}$, 243.1174).

Reactions of 4,4,4-Triphenyl-1-butanol (1), 3,3,3-Triphenyl-1-propanol (2), and 4,4,4-Triphenylbutyric Acid (3) with Lead Tetraacetate. A. 4,4-Diphenylchroman (18) from 2.—A well-stirred mixture of alcohol 2 (1.44 g, 4.99 mmol), lead tetraacetate (4.44 g, 10.0 mmol), and anhydrous benzene (50 ml) was heated in a dry atmosphere at 70 ± 1° for 48 hr. Work-up according to a procedure previously described[2t] gave 1.72 g of semisolid material containing the neutral organic products. Brief extraction of this fraction with a small amount of petroleum ether (bp 30–60°) at room temperature, followed by evaporation of the extract, afforded 1.28 g of solid, which was taken up in a minimum amount of benzene–chloroform. Slow evaporation of the solution at room temperature caused the deposition of 0.35 g (24%) of 18 in the form of large, colorless prisms, mp 172–176°. Recrystallization from methanol gave a product melting at 174–175.5°: ir (CS_2) 1225 cm^{-1} (strong, =CO–), no OH or C=O absorption; nmr ($CDCl_3$), δ 6.5–7.4 (m, 14, C_6H_4 and two C_6H_5), 4.02 (distorted t, 2, $J \approx 5$ Hz, CH_2O), and 2.76 ppm (distorted t, 2, $J \approx 5$ Hz, CH_2CH_2O); mass spectrum (70 eV) m/e 286.1364 (strong; calcd for $C_{21}H_{18}O$, 286.1357), 257.0972 (strong; calcd for $C_{19}H_{13}O$, 257.0966), and 209.0962 (strong; calcd for $C_{15}H_{13}O$, 209.0966).

Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.01; H, 6.47.

B. 4,4,4-Triphenylbutyraldehyde (6) from 1.—A mixture of alcohol 1 (2.00 g, 6.61 mmol), lead tetraacetate (3.08 g, 6.95 mmol), and pyridine (35 ml) was stirred at room temperature for 33 hr (final color, pale orange)[20] and then evaporated. The residue was extracted thoroughly with several portions of benzene at room temperature, and the combined extracts were washed twice with 4% aqueous HCl and once with 1 *N* sodium carbonate solution. Evaporation of the dried organic moiety afforded 2.03 g of brownish solid which yielded only small amounts of impure solid materials (<0.1 g) upon attempted recrystallization from cyclohexane or methanol–water. The remaining material was dissolved in boiling methanol (25 ml), and the solution was stirred vigorously while a solution of sodium metabisulfite (3 g) in water (15 ml) was added rapidly. After 6.7 hr of stirring at ambient temperature, the mixture was filtered, and the recovered solid was washed several times on the filter with methanol and then with ether. An aqueous solution of the solid yielded no organic products after basification with a large excess of 3 *N* sodium carbonate. The filtrate and washings were combined, evaporated to remove the methanol, and extracted once with ether. Addition of a large excess of 3 *N* sodium carbonate to the aqueous phase, followed by extraction with ether and evaporation of the dried ether solution, afforded 0.43 g (22% yield) of crude 6 as a viscous oil that slowly solidified, mp 96–108°. Two recrystallizations of the product from petroleum ether (bp 30–60°) at −10° gave snow-white microcrystals: mp 109.5–110.5°; ir (CS_2) 1735 (strong, C=O), 2720, and 2820 cm^{-1} (both medium, CH of CHO), no OH; nmr (CS_2), δ 9.52 (distorted s, 1, CHO), 7.0–7.2 (m, 15, three C_6H_5), 2.80 (distorted t, 2, $J \approx 7$ Hz, Ph_3CCH_2), and 2.15 ppm (distorted t, 2, $J \approx 7$ Hz, CH_2CHO); mass spectrum (70 eV) m/e 300 (too weak for exact mass measurement; calcd for $C_{22}H_{20}O$, 300), 244.1249 (strong; calcd for $C_{19}H_{16}$, 244.1252), and 243.1172 (strong; calcd for $C_{19}H_{15}$, 243.1174).

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 88.07; H, 6.68.

C. Other Reactions (Table I).—These reactions were run under pure helium or oxygen after freeze–thaw degassing, using the apparatus and procedures already described.[2t] Conversions of Pb^{IV} were incomplete in all experiments except expt 2. Reaction mixtures were worked up by a method used previously[2s] to obtain three fractions: A, the solids removed by an initial filtration; B, the organic acid fraction; and C, the neutral organic products. Acidification of the A fractions with excess hydrochloric acid, followed by thorough extraction with ether, gave no organic products except acetic acid. Compositions of the B fractions were established by melting point determinations and spectral comparisons. The C fractions were analyzed quantitatively by programmed temperature vpc[18] (internal standard method) using pure reference compounds for calibration. Products in C were identified by retention times and by comparing the spectral properties (ir, nmr, ms) of trapped vpc peaks with those of authentic specimens. Rough analyses of the C fractions by nmr gave results that were in satisfactory agreement with the results obtained by vpc. The total gas evolved during one of the duplicate runs of expt 1 was analyzed by isothermal vpc, using a standard procedure developed by the Analytical Research Section of this laboratory. On the basis of retention times the gaseous products were tentatively identified as carbon dioxide (the major constituent), ethylene, methane, and carbon monoxide.

Several unidentified peaks were detected in the chromatograms of the C fractions obtained from alcohol 1; however, these peaks amounted to only about 4–5% (expt 1) or 12–13% (expt 2) of the total peak area. No minor peaks were detected in the chromatogram of the C fraction from expt 3. On the basis of retention times, two of the minor products from 1 could have been acetate 5 and olefin 13; however, trapped vpc fractions supposedly corresponding to these compounds were shown to be complex mixtures by spectral analyses. In any event, the yields of 5 and 13 could have been no more than 1–2%. The presence of a trace of aldehyde 6 among the products of expt 1 was suggested by a small nmr peak at the correct position for the CHO proton. Mass spectral analysis of the total C fraction from expt 1 gave no evidence for the presence of appreciable amounts of materials with molecular weights higher than those of the identified products.

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[19] T. Cuvigny and H. Normant, *Compt. Rend.*, **254**, 316 (1962).

[20] *Cf.* R. E. Partch, *Tetrahedron Lett.*, 3071 (1964).

Small amounts (2–3% yield) of the ethyl ester of **3** were detected in the C fractions from expt 4 and 5. This ester is not considered to be a product of the lead tetraacetate oxidation, since its formation is believed to have been due to the presence of a small amount of ethanol (the recrystallization solvent) in the sample of **3** used for these experiments (nmr analysis of **3** supported this hypothesis). Acetate **5** and ester **27** (see below) were shown to be absent from the products of expt 4 and 5, although a few minor products (unidentified, total yield <1%) were detected in the chromatograms of the C fractions.

In a preliminary experiment, 5.00 mmol each of acid **3**, lead tetraacetate, and pyridine were refluxed in dry benzene (25 ml) for 93.5 hr. Approximately 40% of **3** was converted into indan **8** under these conditions.

In order to confirm the absence of phenyl esters formed by intramolecular rearrangement, the C fractions from two experiments with acid **3** (the run with pyridine just described and a large-scale run similar to expt 4) were "saponified" by boiling for several hours with large excesses of potassium hydroxide in aqueous ethanol. Work-up by a procedure described previously[2b] gave only traces of phenol, which could have come from phenyl acetate (an expected minor by-product derived from the solvent)[4b] rather than from rearrangement products.

In view of the foregoing observations, it is believed that no important products escaped detection in expt 1–5. Mechanical losses during work-up could have had a major effect on the material balances, since the amounts of **1**–**3** used for these experiments were always quite small (*ca.* 0.5 g).

1,1-Diphenylindan (8).—A mixture of 3,3-diphenyl-1-indanone[21] (1.48 g, 5.21 mmol), 85% hydrazine hydrate (3 ml), sodium hydroxide (1.0 g), and ethylene glycol (15 ml) was stirred and heated under a water-cooled condenser for 4 hr at 140–159°. Low-boiling constituents were then allowed to distil, and the temperature was kept at 200° for 9.5 hr while stirring was continued. The mixture was cooled, poured into water (100 ml), and extracted with three 20-ml portions of ether. Evaporation of the dried extracts gave a residue, which was boiled with methanol and filtered to remove a small amount of impure, high-melting solid. Stepwise concentration and cooling of the filtrate yielded more of this solid and eventually caused precipitation of **8** as snow-white crystals, 0.83 g (59%), mp 68–69°. Recrystallization from methanol gave a product melting at 70–70.5° (lit.[22] mp 67–68°): ir (CS_2), no OH or C=O; nmr (CCl_4), δ 6.80–7.24 (m, 14, C_6H_4 and two C_6H_5) and 2.81 ppm (distorted s, 4, CH_2CH_2); mass spectrum (70 eV) *m/e* 270.1424 (strong; calcd for $C_{21}H_{18}$, 270.1408) and 193.1024 (strong; calcd for $C_{15}H_{13}$, 193.1017).

3,3,3-Triphenyl-1-propyl 4,4,4-Triphenylbutyrate (27).—The crude acyl chloride obtained in the usual way from 0.50 g (1.58 mmol) of acid **3** (see method A for the preparation of alcohol **1**) was dissolved in dry benzene (5 ml) and added dropwise during 18 min to an ice-cold, stirred solution of alcohol **2** (0.45 g, 1.56 mmole) in pyridine (4 ml). The reaction vessel was stoppered with a Drierite tube, and after an additional 30 min of stirring in the cold the mixture was allowed to stand at room temperature for 18.5 hr. Water (20 ml) was added, and the product was extracted with 20 ml of benzene in two portions. The combined extracts were washed in succession with cold 5% hydrochloric acid (40 ml in three portions), saturated sodium bicarbonate solution, and water. Evaporation of the dried benzene solution gave 0.91 g of waxy, white solid, which afforded 0.32 g (35%) of ester **27**, mp 170–172°, upon recrystallization from methanol. A further recrystallization (hexane) produced tiny, snow-white crystals: mp 172–173°; ir (CS_2) 1740 (strong, ester C=O), 1186, 1173, 1161 (all strong, individual components of a single broad band, ester C-O-C), and 1035 cm^{-1} (medium, broad, ester C-O-C); nmr (CCl_4), δ 6.9–7.3 (m, 30, six C_6H_5), 3.74 (distorted t, 2, $J \approx 8$ Hz, CH_2O), 2.69–2.96 (m, 4, two Ph_3CCH_2), and 1.93 ppm (highly distorted t, 2, $J \approx 8$ Hz, CH_2CO).

Anal. Calcd for $C_{43}H_{38}O_2$: C, 88.02; H, 6.53. Found: C, 87.98; H, 6.54.

3,3,3-Triphenyl-1-propyl Acetate (5).—In accordance with a procedure similar to that described in the literature,[23] heating of a stirred mixture of alcohol **2** (1.00 g, 3.47 mmol) and acetic anhydride (10 ml) for 110 min at reflux temperature gave ester **5** in essentially quantitative yield, mp 119–119.5°. A single recrystallization from ethanol afforded 0.98 g (85%) of short, flat, almost colorless needles: mp 120.7–121.5° (lit.[23] mp 114–115°); ir (CS_2) 1735 (strong, ester C=O), 1230, and 1031 cm^{-1} (both bands strong and broad, ester C-O-C); nmr ($CDCl_3$), δ 7.04–7.33 (m, 15, three C_6H_5), 3.90 (distorted t, 2, $J \approx 8$ Hz, CH_2O), 2.93 (distorted t, 2, $J \approx 8$ Hz, Ph_3CCH_2), and 1.97 ppm (s, 3, CH_3CO).

4,4,4-Triphenyl-1-butyl Acetate (4).—Reaction of alcohol **1** (1.00 g, 3.31 mmol) with acetic anhydride (10 ml) in the manner just described yielded 1.12 g (98%) of crude **4** in essentially pure form, mp 73.5–75.0°. Recrystallization from petroleum ether (bp 30–60°) gave clusters of white needles that melted at 75–76°; continued heating transformed the melt into a second crystalline modification melting at 95–96°. A further recrystallization of the low-melting form from petroleum ether, using the high-melting form for seeding, gave white platelets: mp 95.5–96.5°; nmr (CCl_4), δ 7.0–7.3 (m, 15, three C_6H_5), 4.03 (t, 2, $J = 7$ Hz, CH_2O), 2.55–2.73 (m, 2, Ph_3CCH_2), 2.03 (s, 3, CH_3CO), and 1.26–1.60 ppm (m, 2, CH_2CH_2O). The ir spectra (CS_2) of the two forms of **4** were identical in every respect; they exhibited strong bands at 1739 (ester C=O) and 1235 cm^{-1} (ester C-O-C), as well as a broad doublet of medium intensity at 1043–1035 cm^{-1} (one band due to ester C-O-C, assignment of other band obscure).

Anal. Calcd for $C_{24}H_{24}O_2$: C, 83.69; H, 7.02. Found: C, 83.87; H, 7.23.

Ethyl 4-Phenoxybutyrate (11).—A stirred mixture of 4-phenoxybutyric acid[24] (50.0 g, 0.277 mol), absolute ethanol (150 ml, 2.56 mol), and concentrated sulfuric acid (5.0 g) was refluxed for 3.0 hr, cooled, concentrated to a volume of approximately 100 ml, and diluted with water (300 ml). The lower (ester) layer was separated, and the aqueous phase was extracted with three 50-ml portions of ether. All organic phases were combined, washed twice with 5% sodium bicarbonate solution, dried, concentrated, and then fractionated through a short spinning-band column to recover 51.5 g (89%) of the desired ester as a colorless oil: bp 112° (1.4 mm) [lit.[25] bp 170–173° (25 mm)]; ir (neat) 1740 (strong, ester C=O), 1247 (strong, broad, =CO–), and 1174 cm^{-1} (strong, broad, ester C-O-C); nmr (CCl_4), δ 7.03–7.27 (m, 2, *m*-H of C_6H_5O), 6.66–6.91 (m, 3, *o*- and *p*-H of C_6H_5O), overlapping 4.05 (qr, $J = 7$ Hz) and 3.92 (t, $J = 6$ Hz) (4, CH_2CH_3 and CH_2OPh, respectively), 2.42 (t, 2, $J = 6$ Hz, CH_2CO), 2.02 (qn, 2, $J = 6$ Hz, CH_2CH_2CO), and 1.20 ppm (t, 3, $J = 7$ Hz, CH_3).

1,1-Diphenyl-4-phenoxy-1-butanol (12).—This experiment was performed under nitrogen. A solution of phenylmagnesium bromide was prepared in the usual way from 4.86 g (0.200 g-atom) of magnesium and 33.40 g (0.213 mol) of bromobenzene in 110 ml of dry ether. Ethyl 4-phenoxybutyrate (20.82 g, 0.100 mol) in dry ether (200 ml) was added to the stirred solution at a rate such that gentle refluxing occurred, and the mixture was stirred and heated under reflux for 1.0 hr after addition was complete. A saturated aqueous solution of ammonium chloride (36 ml) was then added slowly (exothermic reaction caused refluxing) with efficient stirring. When coagulation of the precipitate appeared to be complete, the clear ether layer was separated by decantation, and the precipitate was extracted twice with fresh portions of ether. The ether solutions were combined, dried, and evaporated to give an oil that crystallized and then dissolved upon stirring with boiling hexane. Concentration and cooling of the solution gave two crops of alcohol **12** as clusters of white prisms: mp 87–88° (26.35 g) and 86–87.5° (2.76 g, total yield 91%); mp 88–88.5° after a further recrystallization from petroleum ether (bp 30–60°); ir (CS_2) 3584 (medium, sharp, free OH), 3460 (weak, H-bonded OH), and 1244 cm^{-1} (strong, =CO–); nmr (CCl_4), δ 6.6–7.4 (m, 15, three C_6H_5), 3.81 (t, 2, $J = 6$ Hz, CH_2O), 2.25–2.45 (m, 2, CH_2CPh_2OH), 2.21 (s, 1, OH), and 1.55–1.85 ppm (m, 2, CH_2CH_2O).

Anal. Calcd for $C_{22}H_{22}O_2$: C, 82.98; H, 6.96. Found: C, 82.93; H, 6.98.

In another experiment, crystallization of the crude alcohol from petroleum ether (bp 30–60°) gave a product that melted at 68–69° (fairly rapid heating), solidified upon further heating, and remelted at 87–88°. When heated very slowly this material melted only at the higher temperature, and its nmr spectrum was identical with that of the product having a single melting point.

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[24] W. Reppe, *Ann.*, **596**, 158 (1955).

[25] S. G. Powell and R. Adams, *J. Amer. Chem. Soc.*, **42**, 646 (1920).

2,3,4,5-Tetrahydro-5,5-diphenyl-1-benzoxepin (9).—Polyphosphoric acid (100 g) was placed in a 500-ml indented (Morton) flask equipped with an efficient cone drive stirrer (Teflon paddle). The acid was preheated to 100 ± 1° and stirred very vigorously at this temperature while 10.0 g (31.4 mmol) of finely powdered **12** was added in small portions over a period of 15 min. Rapid stirring at 100 ± 1° was continued for an additional 110 min. The hot, brownish yellow mixture was then poured into 700 ml of ice water, made strongly basic (pH 10) with excess 50% sodium hydroxide solution, and extracted twice with benzene. Evaporation of the dried extracts gave 8.48 g of pale yellow solid, which was mixed well with a minimum amount of petroleum ether (bp 30–60°), cooled to −10°, and filtered to recover 5.24 g of solid. (Work-up of the filtrate yielded none of the desired product.) The solid was boiled and stirred for 3 hr with approximately 2 l. of methanol; and after filtering to remove a small amount of insoluble material, the solution was concentrated to the cloud point and cooled. Small white crystals of **9** precipitated (2.50 g, mp 180–182°); a second crop melting at 179–182° (0.31 g, total yield 30%) was obtained in the usual way. Recrystallization of the first crop from methanol gave tiny, snow-white needles: mp 182.0–182.3°; ir (CS_2) 1220 cm^{-1} (strong, =CO–), no OH or C=O; nmr (CCl_4), δ 6.6–7.3 (m, 13, two C_6H_5 and 7, 8, and 9 H of C_6H_4), 6.28 (dd, 1, J_{ortho} = 8 Hz, J_{meta} = 2 Hz, 6 H of C_6H_4),[26] 3.83 (t, 2, J = 6 Hz, CH_2O), 2.66 (distorted t, 2, $J \approx 6$ Hz, CH_2CPh_2), and 1.87 ppm (distorted qn, 2, $J \approx 6$ Hz, CH_2CH_2O); mass spectrum (70 eV) *m/e* 300.1541 (strong; calcd for $C_{22}H_{20}O$, 300.1514), 223.1122 (medium; calcd for $C_{16}H_{15}O$, 223.1123), and 181.0650 (weak; calcd for $C_{13}H_9O$, 181.0653).

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 88.06; H, 6.75.

4,4-Diphenyl-3-butenyl Phenyl Ether (13).—Treatment of benzene solutions of alcohol **12** with dry HCl or phosphorus pentoxide produced **13** in essentially quantitative yield. Very high yields of **13** also resulted from reactions of **12** with polyphosphoric acid (see above) which were performed with inefficient stirring. In an experiment typifying the most convenient method of synthesis, a solution of **12** (0.50 g, 1.57 mmol) in benzene (10 ml) was placed over Drierite (0.5 g), saturated with dry hydrogen chloride, allowed to stand at room temperature in a stoppered flask for 6 hr, filtered, and evaporated. The nmr spectrum of the crude liquid residue (0.47 g, 100%) was identical with the spectrum of an analytical sample of **13** prepared by distillation of the crude product through a short spinning-band column. The pure material was obtained as a straw-colored oil: bp 179° (0.7 mm); ir (neat) 1243 cm^{-1} (strong, =CO–), no OH; nmr (CCl_4), δ 7.0–7.4 (m, 12, two C_6H_5C and *m*-H of C_6H_5O), 6.68–6.89 (m, 3, *o*- and *p*-H of C_6H_5O), 6.14 (t, 1, J = 7 Hz, $CH_2CH{=}C$), 3.91 (t, 2, J = 7 Hz, CH_2O), and 2.54 ppm (qr, 2, J = 7 Hz, $CH_2CH{=}C$); mass spectrum (70 ev) *m/e* 300.1491 (weak; calcd for $C_{22}H_{20}O$, 300.1514), 207.1174 (medium; calcd for $C_{16}H_{15}$, 207.1174), and 193.1017 (medium; calcd for $C_{15}H_{13}$, 193.1017).

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.94; H, 6.77.

Registry No.—**1,** 16778-07-7; **2,** 15070-88-9; **3,** 16778-09-9; **4,** 16778-10-2; **5,** 16778-11-3; **6,** 16778-12-4; **8,** 16778-13-5; **9,** 16778-14-6; **11,** 2364-59-2; **12,** 16778-16-8; **13,** 16778-17-9; **18,** 16778-18-0; **27,** 16778-19-1; lead tetraacetate, 546-67-8.

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[26] This assignment is based on (a) an examination of a molecular model, which indicates that the proton in question lies near the periphery of the shielding cone of one of the phenyl groups, and (b) a comparison with the nmr spectrum reported for 2,3,4,5-tetrahydro-5,5-dimethyl-1-benzoxepin [H. Hart, J. L. Corbin, C. R. Wagner, and C. Wu, *J. Amer. Chem. Soc.*, **85**, 3269 (1963)], which exhibits no aromatic peaks at δ <6.8.

Mechanisms of Photochemical Reactions in Solution. LIII.[1] Cycloaddition of Carbonyl Compounds to Allenes

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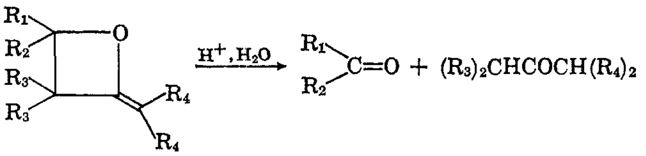
Adlehydes and ketones undergo photochemical cycloaddition reactions to allenes to form oxetanes. The latter will in turn react with the carbonyl compounds forming 1,5- and 2,5-dioxaspiro[3.3]heptane derivatives. In some cases the oxetanes undergo photoisomerization to cyclobutanones. The quantum yield for disappearance of acetophenone in the presence of tetramethylallene was found to be 0.59. A mechanism is proposed involving the addition of carbonyl triplets to the allenes.

Preliminary reports of studies of photochemical cycloaddition of ketones to allenes have recently been reported by Arnold and Glick[2] and by ourselves.[3] The principal products formed in the reactions are shown in Table I along with analytical data and key spectroscopic characteristics. In some instances pinacols derived from the ketones were also isolated. The structures of the addition compounds are indicated by their spectra and by hydrolysis in aqueous acid.



Hydrolytic cleavage of monoadducts (**1**, **4**, **7**, **9**, **11**, **12**, and **17**) gives the original ketone and the ketone that is formally derived by addition of the elements of water to the allene.

The spiro ketal, **8**, is easily cleaved to acetophenone and diisopropyl ketone.

$$8 \xrightarrow{H^+,\ H_2O} 2C_6H_5COCH_3 + (CH_3)_2CHCOCH(CH_3)_2$$

The 2,5-dioxaspiro[3.3]heptanes (**5**, **13**, **14**, and **15**) are not cleaved to ketones by aqueous acid at room temperature.

All of the monoadducts have strong infrared absorption bands at or close to 1735 cm^{-1}. We believe that the band is analogous to absorption of enol ethers found between 1633 and 1712 cm^{-1}.[4] The very high frequency of the absorption is reminiscent of the

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[1] Part LII: B. M. Monroe, S. A. Weiner, and G. S. Hammond, *J. Amer. Chem. Soc.*, **90**, 1913 (1968).

[2] D. A. Arnold and A. H. Glick, *Chem. Commun.*, 813 (1966).

[3] H. Gotthardt, R. Steinmetz, and G. S. Hammond, *ibid.*, 480 (1967).

[4] S. M. McElvain and R. E. Starn, *J. Amer. Chem. Soc.*, **77**, 4571, 5601 (1955).