The Reaction of Triarylmethanols with Lead Tetraacetate. Mechanism of the Lead Tetraacetate Oxidation of Monohydric Alcohols[1]

W. H. Starnes, Jr.

Contribution from the Esso Research and Engineering Company,
Baytown Research and Development Division, Baytown, Texas 77520.
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Abstract: Lead tetraacetate reacts with triphenylmethanol (**1a**), diphenyl(*p*-nitrophenyl)methanol (**1b**), or diphenyl(*p*-methoxyphenyl)methanol (**1c**) in benzene or acetonitrile solution at 82° to form aryloxydiarylmethyl acetates (**2a–e**) in yields ranging up to 91%. Hydrolysis of the acetates under various conditions gives mixtures of phenols, benzophenones, and benzophenone ketals. For reactions with **1b** or **1c**, quantitative analysis of the hydrolysis products by glpc permits the calculation of relative carbon-to-oxygen migratory aptitudes for the itinerant aryl groups. In the case of **1b**, the statistically corrected *p*-nitrophenyl: phenyl migratory ratio is 4.4 ± 0.3. This ratio is independent of solvent composition and is unaffected by the addition of pyridine or copper salts. In the case of **1c**, the statistically corrected *p*-methoxyphenyl: phenyl migratory ratio is strongly dependent upon reaction conditions and has values ranging from 1.1 ± 0.1 to 16 ± 1. Low *p*-methoxyphenyl: phenyl ratios are obtained for reactions run in benzene or in the presence of pyridine and/or copper salts; high ratios are obtained in acetonitrile solution and in experiments where nitrobenzene is added. On the basis of these data and other pertinent facts, mechanisms are proposed for the oxidation of alcohols **1a–c** with lead tetraacetate. Two mechanisms are operative. One is a radical chain process which is initiated by alkoxy radicals derived from the substrate. This process is inhibited by nitrobenzene and catalyzed by copper salts and (possibly) by pyridine. The radical chain mechanism is responsible for the low *p*-methoxyphenyl: phenyl migratory ratios obtained in some of the reactions with **1c**, and it is the only mechanism which is operative during oxidations of **1b** and, probably, of **1a**. The other mechanism, a quasiionic process, occurs to an appreciable extent only with **1c** and is responsible for the high *p*-methoxyphenyl: phenyl ratios obtained with this alcohol under certain conditions. It is suggested that the quasiionic rearrangement may have occurred *via* a concerted, anchimerically assisted decomposition of a lead(IV) alcoholate derived from the substrate. Mechanisms for the oxidation of other types of alcohols with lead tetraacetate are considered briefly in the context of these results.

For many years lead tetraacetate has been recognized as one of the most useful and versatile oxidizing agents available to the organic chemist.[2] Although its ability to oxidize simple monohydric alcohols was noted long ago in the pioneering researches of Criegee,[3] this type of reaction received little attention until 1959, when Cainelli, *et al.*, reported the formation of the tetrahydrofuran ring system in the reaction of lead tetraacetate with a steroidal monohydric alcohol.[4] The obvious synthetic utility of this novel oxidative cyclization prompted its intensive investigation and served as the primary impetus for the great revival of interest in the lead tetraacetate–alcohol reaction which has been apparent in recent years.[5] The reaction is now known to encompass a wide variety of oxidative processes, many of which can be visualized as occurring by way of a reactive intermediate, generated from the hydroxyl function, which is capable of attacking carbon–hydrogen bonds, undergoing β cleavage at an adjacent carbon–carbon single bond, or adding to unsaturated linkages. These processes are all characteristic of alkoxy radicals, and, in fact, many of the final products can be accounted for in terms of radical mechanisms if adequate consideration is given to the possibility that the carbon radicals formed in intermediate stages are rapidly oxidized to carbonium ions (either actual or incipient) under the reaction conditions.[5,6] However, other mechanisms have been considered by various investigators,[5–7] and conclusive evidence for the operation of a radical (or any other) mechanism has not been forthcoming. The present paper deals with a novel reaction of lead tetraacetate which occurs in the triarylmethanol series and is particularly well suited for mechanistic studies. This work has provided con-

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(1) This work was described in a preliminary communication: W. H. Starnes, Jr., *J. Am. Chem. Soc.*, 89, 3368 (1967).

(2) For an authoritative review, see R. Criegee, "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, p 277.

(3) R. Criegee, L. Kraft, and B. Rank, *Ann.*, 507, 159 (1933).

(4) G. Cainelli, M. L. Mihailović, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, 42, 1124 (1959).

(5) *Cf.* the review by K. Heusler and J. Kalvoda, *Angew. Chem. Intern. Ed. Engl.*, 3, 525 (1964).

(6) See, *inter alia*, (a) G. Cainelli, B. Kamber, J. Keller, M. L. Mihailović, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **44**, 518 (1961); (b) M. Amorosa, L. Caglioti, G. Cainelli, H. Immer, J. Keller, H. Wehrli, M. L. Mihailović, K. Schaffner, D. Arigoni, and O. Jeger, *ibid.*, **45**, 2674 (1962); (c) K. Heusler, J. Kalvoda, G. Anner, and A. Wettstein, *ibid.*, 46, 352 (1963); (d) K. Heusler and J. Kalvoda, *ibid.*, 46, 2732 (1963); (e) D. Hauser, K. Schaffner, and O. Jeger, *ibid.*, 47, 1883 (1964); (f) D. Hauser, K. Heusler, J. Kalvoda, K. Schaffner, and O. Jeger, *ibid.*, 47, 1961 (1964); (g) K. Heusler, *Tetrahedron Letters*, 3975 (1964); (h) V. M. Mićović, R. I. Mamuzić, D. Jeremić, and M. L. Mihailović, *Tetrahedron*, 20, 2279 (1964); (i) M. Stefanović, M. Gaŝić, L. Lorenc, and M. L. Mihailović, *ibid.*, 20, 2289 (1964); (j) M. L. Mihailović, Z. Maksimović, D. Jeremić, Ž. Čeković, A. Milovanović, and L. Lorenc, *ibid.*, 21, 1395 (1965); (k) M. L. Mihailović, Ž. Čeković, Z. Maksimović, D. Jeremić, L. Lorenc, and R. I. Mamuzić, *ibid.*, 21, 2799 (1965); (l) M. L. Mihailović, Ž. Čeković, and D. Jeremić, *ibid.*, 21, 2813 (1965); (m) M. L. Mihailović and M. Miloradović, *ibid.*, 22, 723 (1966); (n) M. L. Mihailović, J. Bošnjak, Z. Maksimović, Ž. Čeković, and L. Lorenc, *ibid.*, 22, 955 (1966); (o) R. E. Partch, *J. Org. Chem.*, 30, 2498 (1965); (p) J. Lhomme and G. Ourisson, *Chem. Commun.*, 436 (1967).

(7) (a) W. A. Mosher and H. A. Neidig, *J. Am. Chem. Soc.*, 72, 4452 (1950); (b) A. Bowers and E. Denot, *ibid.*, 82, 4956 (1960); (c) J. K. Kochi, *ibid.*, 87, 3609 (1965); (d) M. S. Kharasch, H. N. Friedlander, and W. H. Urry, *J. Org. Chem.*, 16, 533 (1951); (e) W. A. Mosher, C. L. Kehr, and L. W. Wright, *ibid.*, 26, 1044 (1961); (f) S. Moon and J. M. Lodge, *ibid.*, 29, 3453 (1964); (g) R. M. Moriarty and K. Kapadia, *Tetrahedron Letters*, 1165 (1964).

Table I. Reactions of Triarylmethanols with Lead Tetraacetate[a]

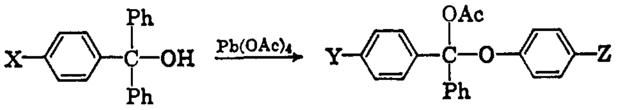
Expt	Meth-anol[b]	Solvent[c]	Additives, mmol	Time, hr	Hydrol method[d]	Yield,[e] mol/mol of **1a–c** Ph_2CO	Yield,[e] mol/mol of **1a–c** *p*-XPh_2CO	Mig apt[f] *p*-XPh:Ph
1[g]	**1a**	PhH	. . .	95	Basic	0.599[h]	. . .	. . .
2	**1a**	PhH	. . .	95	Basic[i]	0.773[j]	. . .	. . .
3	**1a**	PhH	. . .	95	Acidic	0.911	. . .	. . .
4	**1a**	PhH	$PhNO_2$, 0.327	95	Acidic	0.575	. . .	. . .
5	**1a**	PhH	$PhNO_2$, 3.27	95	Acidic	0.264	. . .	. . .
6	**1a**	PhH	O_2[k]	96	Acidic	0.761	. . .	. . .
7[g,l]	**1a**	PhH[m]	Py,[n] 19.7	22	Basic[i]	0.232 ±0.007[o]	. . .	. . .
8[g,l]	**1a**	PhH[m]	Py,[n] 19.7	22	Acidic	0.272	. . .	. . .
9[g]	**1a**	MeCN	. . .	95	Basic[i]	0.072	. . .	. . .
10	**1a**	MeCN	. . .	95	Acidic	0.072	. . .	. . .
11[g,p]	**1b**	PhH	. . .	119	Acidic	0.0575	0.0267	4.3
12	**1b**	PhH	. . .	95	Acidic	0.104	0.0506	4.1
13[g,l]	**1b**	PhH[m]	Py,[n] 19.7	22	Acidic	0.174 ±0.004[q]	0.0805 ±0.0001[q]	4.3 ±0.1[q]
14[l]	**1b**	PhH[m]	Py,[n] 19.7 Cu salt,[r] 1.00	1.3	Acidic	0.0912	0.0389	4.7
15	**1b**	MeCN	. . .	97	Acidic	0.0438	0.0204	4.3
16[g]	**1b**	MeCN	. . .	122	Acidic	0.0754	0.0346	4.4
17[g]	**1b**	MeCN	. . .	187	Acidic	0.0875	0.0415	4.2
18	**1b**	MeCN	$Cu(OAc)_2 \cdot H_2O$, 1.00	25	Acidic	0.0686	0.0291	4.7
19[g]	**1c**	PhH	. . .	95	Basic	0.396	0.199	4.0
20	**1c**	PhH	. . .	95	Basic	0.370	0.218	3.4
21	**1c**	PhH	O_2[k]	95	Basic	0.380	0.225	3.4
22	**1c**	PhH	$PhNO_2$, 3.27	100	Acidic	0.570	0.0934	12
23	**1c**	PhH	$PhNO_2$, 6.54	95	Acidic	0.681	0.100	14
24[g,l]	**1c**	PhH[m]	Py,[n] 19.7	24	Basic	0.194 ±0.009[q]	0.204 ±0.005[q]	1.9 ±0.1[q]
25[g,l]	**1c**	PhH[m]	Py,[n] 19.7	23	Basic[i]	0.226	0.287	1.6
26[g,l]	**1c**	PhH[m]	Py,[n] 19.7	29	Acidic	0.183	0.246	1.5
27	**1c**	PhH	Cu salt,[r] 1.00	23	Basic	0.194	0.335	1.2
28	**1c**	PhH	Cu salt,[r] 1.00	22	Acidic	0.211	0.351	1.2
29[l]	**1c**	PhH[m]	Py,[n] 19.7; Cu salt,[r] 1.00	1.4	Basic	0.0908	0.156	1.2
30[l]	**1c**	PhH[m]	Py,[n] 19.7; Cu salt,[r] 1.00	1.6	Acidic	0.0802	0.168	1.0
31	**1c**	MeCN	. . .	95	Basic	0.578	0.0883	13
32	**1c**	MeCN	$PhNO_2$, 6.54	95	Acidic	0.464	0.0590	16
33	**1c**	MeCN	O_2[k]	95	Basic	0.449	0.0699	13
34[g]	**1c**	MeCN	Py,[n] 14.5	19	Basic	0.202	0.122	3.3
35[g]	**1c**	MeCN	$Cu(OAc)_2 \cdot H_2O$, 1.00	95	Basic	0.357	0.220	3.2
36	**1c**	MeCN	$Cu(OAc)_2 \cdot H_2O$, 1.00	22	Basic	0.365	0.205	3.6
37	**1c**	MeCN	Py,[n] 14.5 $Cu(OAc)_2 \cdot H_2O$, 1.00	18	Basic	0.0977	0.153	1.3

[a] $Pb(OAc)_4$, 7.22 mmol (unless noted otherwise); $CaCO_3$, 15.0 mmol (used in all experiments except those with pyridine); 82 ± 2°. All experiments run under nitrogen or helium after freeze–thaw degassing unless noted differently. [b] **1a** or **1c**, 3.27 mmol; **1b**, 3.28 mmol. [c] 20 ml unless noted otherwise. [d] Done at ambient temperature unless noted otherwise. See Experimental Section for details. [e] Yields of ketals included. [f] $2[Ph_2CO]/[p\text{-}XPh_2CO]$. [g] Run under nitrogen without preliminary degassing. [h] Includes methoxyphenoxydiphenylmethane, 0.164 mol/mol of **1a**. [i] Done at reflux temperature. [j] Includes (mol/mol of **1a**) methoxyphenoxydiphenylmethane (0.282) and dimethoxydiphenylmethane (0.186). [k] Run under pure O_2 atmosphere after freeze–thaw degassing. [l] $Pb(OAc)_4$, 9.83 mmol. [m] 25 ml. [n] Pyridine. [o] Average of two runs; includes methoxyphenoxydiphenylmethane, 0.014 ± 0.004 mol/mol of **1a**. [p] $Pb(OAc)_4$, 3.61 mmol. [q] Average of two runs. [r] Harshaw "Uversol copper liquid 8%" (an organic-soluble copper carboxylate).

siderable insight into the mechanism of oxidation of monohydric alcohols with lead tetraacetate,

Results

Triphenylmethanol (**1a**) reacts with lead tetraacetate[8] in hot benzene or acetonitrile (*cf*, Table I) to form hemiketal acetate **2a**. Attempts to isolate a pure sample



1a, X = H
b, X = NO_2
c, X = OMe

2a, Y = Z = H
b, Y = H; Z = NO_2
c, Y = NO_2; Z = H
d, Y = H; Z = OMe
e, Y = OMe; Z = H

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(8) (a) The only previous attempt to oxidize a triarylmethanol with lead tetraacetate appears to have been that of Cordner and Pausacker,[8b] who reported that the reagent "remained unchanged in the presence of . . . triphenylmethanol." Although details are not given, other data in their published account suggest that the experiment was done in acetic acid solution at a temperature near the ambient range. (b) J. P. Cordner and K. H. Pausacker, *J. Chem. Soc.*, 102 (1953). (c) Mosher and Neidig[7a] found that reaction of 1,2,2,2-tetraphenylethanol with lead tetraacetate in acetic acid–acetic anhydride gave **1a**, but no products resulting from its subsequent conversion were reported.

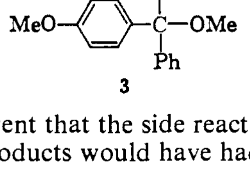
of **2a** have been unsuccessful due to the low hydrolytic stability of the compound and to difficulties encountered in attempts to separate it from residual amounts of the starting alcohol using customary work-up procedures. However, the presence of **2a** is conclusively established by the following observations. The infrared spectra (Nujol) of crude reaction mixtures (examined after removal of metal salts and acetic acid) show characteristic ester carbonyl absorption at 1760 cm^{-1}, together with three strong bands at 1235, 1221, and 1206 cm^{-1} which do not appear in the spectrum of **1a** and are assignable to C–O vibrations. A sharp singlet arising from the protons of the acetoxy group appears in the nmr spectra of these mixtures at τ 8.08 (CCl_4 solution). Furthermore, the chemical ionization mass spectrum[9] of a typical mixture shows a weak MW + 1 peak at *m/e* 319, as well as peaks at *m/e* 259 (strong) and 225 (weak) which can easily be accounted for by loss of acetic acid and phenol, respectively, from the protonated parent species. These peaks do not appear in the spectra of **1a** or any of the possible hydrolysis products of the hemiketal ester. Hydrolysis of crude reaction mixtures with HCl in aqueous tetrahydrofuran gave benzophenone, phenol, and acetic acid, which are the products expected to result from **2a** under these conditions. Finally, treatment of a crude reaction mixture with methanol produced methoxyphenoxydiphenylmethane, and saponification of crude mixtures with potassium hydroxide in aqueous methanol gave methoxyphenoxydiphenylmethane and dimethoxydiphenylmethane in addition to benzophenone, phenol, and acetic acid.

Quantitative glpc analyses of the hydrolysis products showed that the only other material present in appreciable quantity was the starting alcohol. Phenol recoveries were not quantitative, although they amounted to 80–90% of the total yield of benzophenone (ketone plus ketals) in some experiments. The low recoveries of phenol may have been due to volatilization losses and to air oxidation of the compound during continuous ether extraction (see Experimental Section). However, in a run similar to experiments 1–3 (102-hr reaction time) glpc examination of the product mixture prior to hydrolysis showed that approximately 30% of the hemiketal acetate had undergone conversion to diphenoxydiphenylmethane. This observation can be taken as evidence for the slow production of phenol or phenoxide ion from the acetate during the long reaction period, and, if this is the case, a part of the observed phenol losses may well have been due to the formation of acetoxycyclohexadienones (or other relatively volatile compounds), which might have escaped detection by the analytical procedure.[10] In any event, control experiments using standard mixtures of the hydrolysis products showed that most (perhaps all) of the phenol losses could have occurred during work-up procedures. No rigorous attempts to minimize these losses were made, since the control runs also showed that total recoveries of benzophenone (free ketone plus ketals) were essentially quantitative in all cases and, therefore, would serve as an excellent measure of the extent of reaction.

The conversion of **1a** to **2a** must involve intramolecular rearrangement of a reactive intermediate formed from the hydroxyl group; this point is considered at length in the Discussion. In order to determine the nature of the rearranging species, lead tetraacetate reactions were carried out with alcohols **1b** and **1c** (Table I). Hydrolysis of the mixtures of hemiketal acetates (**2b,c**, or **2d,e**) formed in these experiments gave mixtures containing phenols, benzophenones, and, in some cases (basic hydrolysis in methanol–water), the corresponding ketals. Basic hydrolysis was unsatisfactory for the product mixtures resulting from **1b**, since under these conditions *p*-nitrobenzophenone was converted into other products. These products were not identified, although their mode of formation was confirmed by a control experiment. In experiments with **1c** the only ketals formed in appreciable amount were the dimethyl compounds. Yields of the benzophenone ketal were uniformly low (0–5% of the total benzophenone fraction), while yields of the *p*-methoxybenzophenone ketal were quite high in some cases (up to 88% of the total *p*-methoxybenzophenone fraction). Since the hydrolytic stability of the *p*-methoxy ketal is much less than that of the unsubstituted one, the difference in ketal yields must be attributed to a rate-enhancing effect of the methoxy substituent on the nucleophilic displacement reaction(s) of **2e**.

Although the extents of conversion obtained with alcohol **1b** were always relatively low, glpc analyses of the hydrolysates showed only traces of other materials in addition to the expected hydrolysis products and unconverted **1b**. In a few experiments with **1b** quantitative glpc analyses for the starting alcohol were performed, and the results confirmed the nonexistence of side reactions in this system.

The reactions of **1c** with lead tetraacetate were somewhat less clean, side products amounting to 5–15% (glpc area) of the neutral product fraction being formed. No extraneous materials were detected by glpc in the phenolic fractions. One of the neutral by-products (0–0.08 mol/mol of **1c**) appeared only in experiments where basic hydrolysis was employed; it was shown to be compound **3** by spectral measurements on a trapped glpc fraction (see Experimental Section). The acetate of **1c** would seem to be a plausible precursor for this ether;[11] however, a control experiment showed that a small amount of the ether could be produced directly from the starting alcohol under the hydrolysis conditions employed. A second by-product from **1c** (0.01–0.15 mol/mol) was shown to be quinone methide **4** by comparisons with an authentic specimen. It is apparent that the side reactions leading to the identified by-products would have had no effect on measurements of the relative migratory aptitudes of the aryl groups. The other side reactions could have influenced these



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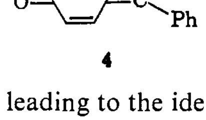

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[9] For descriptions and discussions of chemical ionization mass spectrometry, see M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **88**, 2621, 4337 (1966), and later papers by these authors.

[10] Large glpc peaks due to solvent could have masked smaller peaks arising from materials with comparably low retention times. See ref 2, pp 288–292, and literature cited therein, for information regarding the lead tetraacetate oxidation of phenols.

[11] Conversion of starting alcohol to the corresponding acetate is a common side reaction in lead tetraacetate oxidations. For representative examples, see ref 6e,f,h,j–p, and 7b,e,f.

measurements to only a minor extent (if at all), since the yields of the unidentified by-products[12] were always quite low (totaling *ca.* 1–5 glpc area %).

The relative migratory aptitudes listed in Table I were calculated from the yields of ketones and ketals. Calculations based on yields of phenols were less satisfactory, as recoveries of phenols were not always quantitative. For this reason, the yields of phenols were not determined in all of the tabulated experiments. However, for those runs with alcohol **1c** where the necessary data were obtained, it was found that migratory aptitudes calculated from phenol yields were in good qualitative agreement with the values computed in the preferred manner. Large losses of (unsubstituted) phenol occurred in the experiments with **1b**, whereas *p*-nitrophenol recoveries were essentially complete in all of the cases examined. Control experiments with standard mixtures showed that migratory aptitudes calculated by the preferred method were never in error by more than *ca.* ±8% of the values given, and that the losses of phenols observed in experiments with **1b** or **1c** could have occurred during work-up of the hydrolysates.

Discussion

Mechanism of the Oxidation of Triarylmethanols. The relative migratory aptitudes for *p*-nitrophenyl *vs.* phenyl obtained in experiments 11–18 are all identical within experimental error, and they are consistent with the operation of a homolytic rearrangement mechanism. The average value of 4.4 ± 0.3 may be compared with the (statistically corrected) *p*-nitrophenyl:phenyl migratory ratio of *ca.* 6–8 obtained by Bartlett and Cotman in their study of the thermal decomposition of diphenyl(*p*-nitrophenyl)methyl hydroperoxide, which was believed to proceed *via* a homolytic route.[13] Taking into consideration the analytical difficulties they encountered and the fact that their reaction was not particularly clean, the agreement between their result and ours is quite satisfactory. In contrast, the ionic, acid-catalyzed decomposition of diphenyl(*p*-nitrophenyl)methyl hydroperoxide has been reported to give phenyl migration exclusively,[13,14] and a similar result has been obtained for the ionic decomposition of the corresponding perbenzoate.[15] It should be noted that the literature contains several other examples of reactions where the nitro group has been found to accelerate the rate of radical attack at the *para* position of a benzene ring; these include homolytic aromatic phenylation,[16] the homolytic neophyl rearrangement,[17] and the rearrangement of the 2,2-diphenyl-2-(*p*-nitrophenyl)ethyl radical.[18] Also pertinent to the point in question are the peculiar results reported for the thermal decompositions of *t*-butyl diphenyl(*p*-nitrophenyl)methyl peroxide[19,20] and bis[diphenyl(*p*-nitrophenyl)methyl] peroxide.[20] The mechanisms of these decompositions are quite complex (for a possible explanation, see below), but the products are not inconsistent with the idea that preferential migration of *p*-nitrophenyl occurs during rearrangement of the diphenyl(*p*-nitrophenyl)methoxy radical.

That the lead tetraacetate oxidation of **1b** does not proceed *via* competing radical and ionic mechanisms is shown by the insensitivity of the migratory ratio to solvent polarity (experiments 11, 12, and 15–17) and, especially, by the results of experiments 13, 14, and 18. Pyridine (experiment 13) strongly accelerates the over-all rate of disappearance of lead(IV) in a manner analogous to that observed in oxidative decarboxylations of aliphatic acids with lead tetraacetate.[7c] However, the increase in rate is not accompanied by a dramatic increase in the yield of products derived from the alcohol. This observation is not surprising, for it simply suggests that the rate of the pyridine-catalyzed decomposition of lead tetraacetate itself is comparable to the rate of formation of the lead(IV) alcoholate (**5**) whose decomposition is believed to be involved in the alcohol oxidation reaction.[21] It has been suggested that the homolysis of lead(IV) tetracarboxylates is accelerated by coordination with pyridine,[7c] and some evidence in support of this suggestion has been presented.[7c,22a]

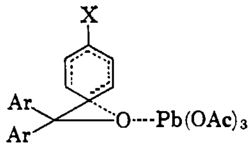
$Ar_3COPb(OAc)_3$

5

$Ar_3COPb(OAc)_3Py_n$

6

$n = 1, 2$, etc.



7, X = NO_2, H, or OMe

If this idea is correct, homolysis of a species such as **5** should be accelerated by pyridine in a similar manner.[22b] However, even if this proves not to be the case, the formation of coordination complexes such as **6** should cause the lead atom to acquire considerable negative charge and, for that reason, should greatly retard decomposition *via* a heterolytic ("oxonium") route. Therefore, the failure of pyridine to affect the *p*-nitro-

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(12) (a) The unidentified materials may have resulted from attack of the *p*-methoxyphenyl nucleus by lead tetraacetate. See (b) D. R. Harvey and R. O. C. Norman, *J. Chem. Soc.*, 4860 (1964).

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(16) (a) D. H. Hey, S. Orman, and G. H. Williams, *J. Chem. Soc.*, 565 (1961); (b) R. Itô, T. Migita, N. Morikawa, and O. Simamura, *Tetrahedron*, 21, 955 (1965).

(17) C. Rüchardt and R. Hecht, *Ber.*, **98**, 2471 (1965).

(18) D. Y. Curtin and J. C. Kauer, *J. Org. Chem.*, **25**, 880 (1960).

(19) M. S. Kharasch, A. C. Poshkus, A. Fono, and W. Nudenberg, *ibid.*, 16, 1458 (1951).

(20) J. I. G. Cadogan, D. H. Hey, and W. A. Sanderson, *J. Chem. Soc.*, 5236 (1961).

(21) (a) An alternative explanation is that decomposition of **6** involves more acetoxy cleavage than does the decomposition of **5**. If this were the case, appreciable amounts of $Pb(OCAr_3)(OAc)$ should have been present in the lead(II) product fraction, unless, of course, the alcoholate moiety were exchanged for acetate under the reaction conditions. No evidence for the presence of lead(II) alcoholates was obtained, although it must be emphasized that this possibility was not thoroughly checked. In this connection it is noteworthy that lead diacetate has been reported to be the sole constituent of the lead(II) fractions recovered from the oxidation of simple aliphatic alcohols with lead tetraacetate in the presence of pyridine.[6o] (b) For discussions of the evidence for the intermediacy of **5**, see ref 2, 5, 6j,o, and references cited therein. In the present author's opinion, a mechanism involving homolytic removal of the hydroxyl hydrogen [either directly or following electron transfer from hydroxyl to lead(IV) or lead(III)] has not yet been rigorously excluded on experimental grounds, although direct abstraction seems unlikely in view of the very high energy of the OH bond (C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press Inc., New York, N. Y., 1962, p 136).

(22) (a) J. K. Kochi, *J. Org. Chem.*, 30, 3265 (1965). (b) Lead tetraacetate oxidation of 1-butanol to butanal has recently been shown to proceed *via* a heterolytic mechanism in the presence of pyridine at 30° [R. Partch and J. Monthony, *Tetrahedron Letters*, 4427 (1967)]. However, this result does not rule out the possibility that pyridine catalyzes the *homolytic* decomposition of lead(IV) alcoholates at higher temperatures, particularly in cases where oxidation to the corresponding carbonyl compound is structurally impossible.

phenyl:phenyl migratory ratio is strong evidence against the incursion of an ionic rearrangement process.

The results obtained in the experiments with copper salts are also inconsistent with the operation of a twofold mechanism in the oxidation of **1b**. Cupric acetate strongly accelerates the rate of disappearance of lead(IV) (experiment 18), and the rate is even faster when pyridine and a soluble copper salt[23] are used conjunctively (experiment 14).[24] Rapid destruction of lead tetraacetate itself may again be responsible for the lack of correlation between reaction rate and the alcohol conversions obtained in the presence of the additives. Strong evidence has been presented for the operation of a radical chain mechanism in the copper salt catalyzed decomposition of lead(IV) tetracarboxylates,[7c] and one would certainly expect the decomposition of a species such as **5** to be catalyzed in a similar manner. Indeed, independent evidence for copper salt catalysis of the lead tetraacetate–alcohol reaction has recently been obtained by other workers.[25] In view of these considerations, the migratory ratios obtained in experiments 14 and 18 constitute further good evidence against the operation of competing radical and ionic mechanisms in the oxidation of the nitro alcohol.

The possibility that the lead tetraacetate induced rearrangement of **1b** is a concerted homolytic process (*cf.* 7) is also inconsistent with the extant data. If such a process were operative, the migratory ratio should depend to some extent on the nature of the leaving group. In fact, such a dependence is not observed, in that the same ratios are obtained in the presence of pyridine (where formation of **6** seems highly probable) as in the other cases.[26]

In summary, it appears that the reaction of alcohol **1b** with lead tetraacetate proceeds exclusively by way of the corresponding alkoxy radical.[27]

As regards the detailed mechanism by which the rearrangement of triarylmethoxy radicals occurs, there is good evidence in favor of a true intramolecular process proceeding *via* a bridged transition state (or intermediate). The alternate possibility is a dissociation–recombination mechanism involving two discrete steps: (1) cleavage of the alkoxy radical into diaryl ketone and aryl radical, followed by (2) addition of the aryl radical to the ketonic carbonyl group to produce a rearranged species. However, unless steps 1 and 2 occur entirely within a solvent "cage" and with complete selectivity (which seems highly unlikely in view of the relatively low reactivity of carbonyl groups toward radical additions), this mechanism also predicts that products resulting from reactions of the aryl radicals with the surrounding medium should be observed. In fact, such products could have been formed to only a minor extent, at most, in the reactions of Table I.[28] Further evidence against the cleavage reaction of the two-step mechanism was provided by infrared analyses of crude reaction mixtures; these measurements showed that, in many cases, benzophenones were not present prior to hydrolysis.[29] Finally, it is noteworthy that other investigators have obtained no conclusive evidence for the β cleavage of triarylmethoxy radicals in solution at moderate temperatures.[30]

In striking contrast to the results obtained with alcohol **1b**, the data of Table I clearly show that *two* mechanisms are operative in the reaction of alcohol **1c** with lead tetraacetate. The effects of pyridine and copper salts on reaction rate and product yields are similar to the effects observed with **1b**, and the decreases in the *p*-methoxyphenyl:phenyl migratory ratio caused by these additives are consistent with the incursion of increasing amounts of a homolytic process. The low ratio obtained in experiments 27 and 28 probably reflects the exclusive operation of this type of mechanism, since no further lowering of the ratio occurs (within experimental error) upon addition of pyridine (experiments 29 and 30). In agreement with this conclusion, it is noteworthy that a *p*-methoxyphenyl:phenyl migratory ratio of 0.94 has been reported for the homolytic rearrangement of radicals generated by thermal decomposition of bis[diphenyl(*p*-methoxyphenyl)methyl] peroxide in refluxing benzene.[31] Also of interest in this connection are the similar migratory tendencies of the *p*-methoxyphenyl and phenyl groups in the homolytic neophyl rearrangement[32] and the comparable reactivities of the *para* position of anisole and a nuclear position in benzene toward homolytic phenylation.[16b,33]

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[23] $Cu(OAc)_2\cdot H_2O$ is too insoluble in benzene to exert any catalytic effect in this solvent.

[24] Judging from the rate of gas evolution, this reaction was essentially complete within approximately 15 min.

[25] G. Cainelli and F. Minisci, *Chim. Ind.* (Milan), **47**, 1214 (1965); G. Cainelli and S. Morrocchi, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.*, 40, 464, 591 (1966).

[26] It might also be argued that the operation of a concerted homolytic mechanism would have caused the migratory ratio to be changed by the addition of copper salts, owing to changes in the relative amounts of rearrangement occurring during the initiation and propagation steps and, perhaps, to changes in the nature of the departing (lead-containing) species. The validity of this argument cannot be assessed in the absence of further information, particularly with regard to kinetic chain lengths.

[27] The degree of kinetic freedom associated with this radical cannot be specified at the present time.

[28] Any aryl radicals formed in these systems should either react with solvent (to form biaryls, when the solvent is benzene) or undergo conversion to aryl acetates upon oxidation with lead(IV) or lead(III). In some of the experiments with alcohol **1a**, traces of materials having the correct retention times for biphenyl and phenyl acetate were detected by careful glpc analysis of unhydrolyzed reaction mixtures. However, the yields of these products were too low to permit their separation and conclusive identification, and the possibility that they were formed from solvent-derived phenyl radicals cannot be excluded.

[29] Appreciable amounts of benzophenones were detected prior to hydrolysis in certain experiments where long reaction times were employed. However, slow destruction of the first formed hemiketal acetates is believed to have occurred in these cases (see Results section).

[30] *Cf.* H. Wieland, *Ber.*, **44**, 2550 (1911); M. A. Spielman, *J. Am. Chem. Soc.*, **57**, 1117 (1935); M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **15**, 763 (1950); and ref 19. In contrast, S. J. Cristol and J. E. Leffler [*J. Am. Chem. Soc.*, 76, 4468 (1954)] have suggested a mechanism for the thermal decomposition of triphenylmethyl nitrate which involves β scission of the triphenylmethoxy radical. However, their products can also be accounted for by the mechanism proposed by M. F. Hawthorne [*ibid.*, 77, 5523 (1955)] for decomposition of tris(*p*-nitrophenyl)methyl nitrate, which involves rearrangement of the corresponding triarylmethoxy radical rather than its cleavage. The failure of Cristol and Leffler to find products derived from the radical $(Ph)_2\dot{C}OPh$ may have been due to analytical difficulties or to the fact that NO_2 (an electrophilic species) is a better scavenger for this radical than it is for the corresponding, negatively substituted carbon radical generated in Hawthorne's experiment. Preferential rearrangement of the triphenylmethoxy radical is also supported by thermochemical calculations, which show that rearrangement is exothermic by 1.5 kcal/mol, whereas cleavage is endothermic by 7.9 kcal/mol [P. Gray and A. Williams, *Trans. Faraday Soc.*, **55**, 760 (1959)]. With regard to the possible β scission of triphenylmethoxy radical at very high temperatures, see K. D. Berlin, L. H. Gower, B. S. Rathore, G. P. Sturm, J. W. White, J. B. Richards, and M. Peterson, *J. Org. Chem.*, **28**, 2039 (1963); K. D. Berlin and B. S. Rathore, *ibid.*, **29**, 993 (1964); and K. D. Berlin and G. P. Sturm, *J. Chem. Soc.*, 2275 (1964).

[31] R. M. McNeer, Ph.D. Thesis, University of Chicago, 1953.

[32] Under various conditions *p*-methoxyphenyl:phenyl reactivity ratios ranging from 0.35 to 1.2 have been obtained. *Cf.* C. Rüchardt, *Ber.*, **94**, 2609 (1961); C. Rüchardt and H. Trautwein, *ibid.*, **96**, 160 (1963); and ref 17.

On the other hand, predominant operation of a quasiionic rearrangement mechanism is indicated by the high migratory ratios obtained in experiments 22, 23, and 31–33. Although the nature of the rearranging species involved in this mechanism has not been established conclusively, the most reasonable possibility is that the process occurs *via* a bridged transition state, **7** (X = OMe), having considerable dipolar character. This mechanism has the advantage of requiring no new intermediates and finds a close intermolecular analogy in the mechanism suggested for electrophilic acetoxylation of anisole with lead tetraacetate.[12b] A choice between homolytic and heterolytic transition states for the quasiionic rearrangement cannot be made on the basis of the migratory aptitude data alone.[34] However, if the process is homolytic, it must comprise the initiation step of a radical chain mechanism (see below) whose kinetic chain length is only about one in benzene solution (experiment 19).[35] Since this chain length seems unreasonably low, the heterolytic transition state is currently the preferred one, although it must be emphasized that the other alternative has not been conclusively rejected.

The increased *p*-methoxyphenyl:phenyl migratory ratios obtained in the presence of nitrobenzene (experiments 22, 23, and 32) are of considerable mechanistic significance. The increases were not due to a selective acceleration of the quasiionic mode of reaction, since nitrobenzene caused no marked enhancements in reaction rate and, in any event, would not have changed the polarities of the reaction media to a significant extent at the low concentration levels employed. In fact, qualitative comparisons based on the amounts of lead dioxide formed during work-up indicated that over-all rates of lead(IV) disappearance were, if anything, slower when nitrobenzene was present. Furthermore, the increased ratios obtained in experiments 22 and 23 are too large to be accounted for simply by enhancements in the rate of the quasiionic process. For example, simple calculations[35] show that the migratory ratio obtained in experiment 22 corresponds to only 3% reaction *via* the radical mechanism, whereas 40% of the reaction occurred by this mechanism in experiment 19. Since the total yields of ketones obtained in these two experiments are closely comparable, it is clear that either (a) the rate of the radical process was drastically reduced by nitrobenzene, or (b) in the presence of the nitro compound, considerable amounts of side products were formed in radical scavenging reactions. The latter explanation would apply in the event that a radical, *nonchain* mechanism were competing with a heterolytic quasiionic process, in which case the over-all rate of alcohol conversion would not be decreased by radical scavenging. However, this explanation is excluded by our failure to detect any new products in experiment 22 (or experiment 23) and by the fact that in these experiments the over-all material balances (based on starting alcohol) did not differ significantly from those obtained in experiments 19 and 20. Retardation of the rate of thermal homolysis of **5**, owing to formation of a coordination complex involving the nitro group, is not a reasonable explanation for the nitrobenzene effect, since our results with pyridine and the observations of other workers[7c,22a,36] indicate that coordination should actually favor the homolytic path. It appears, therefore, that nitrobenzene must function as a trapping agent for radicals which, in the absence of the scavenger, are involved in an *induced chain decomposition* of **5**. Similarly, the failure of nitrobenzene to reduce the total yields of ketones in experiments 22 and 23 can be ascribed to prevention by the scavenger of a competing side reaction (radical-induced decomposition) which destroys lead tetraacetate itself. Operation of a radical chain mechanism in the decomposition of **5** seems eminently reasonable in view of the good evidence for occurrence of a similar process during oxidative decarboxylations with lead tetraacetate.[7c]

The ability of nitrobenzene to inhibit the oxidation of **1c** is not without precedent, for nitrobenzene is known to be an efficient scavenger for carbon radicals which are highly stabilized by resonance.[37] *A priori*, the inhibition might involve formation of a loose π complex,[37c,38] addition of radicals to the ring or the nitro group,[37c,39] or radical oxidation.[37b] In the present case an oxidation mechanism is the most attractive possibility, since electron transfer to nitrobenzene and other nitro compounds from carbon radicals bearing α OR or OH groups is known to occur quite readily.[40] Oxidation of radicals such as $Ar_2\dot{C}OAr$ and the bridged radicals corresponding to **7** should be particularly facile in view of the very high thermodynamic stabilities of the corresponding carbonium ions, and such reactions may well have been responsible for some of the peculiar results reported in the literature (in particular, the absence of coupling products derived from $Ar_2\dot{C}OAr$) for decompositions of *p*-nitrotriarylmethyl peroxides.[13,19,20] Our failure to find products formed in inhibition reactions may have been due to analytical difficulties, low yields, or the occurrence of a cyclic inhibition sequence such

$$PhNO_2 + R\cdot \longrightarrow PhNO_2\cdot^- + R^+ \tag{1}$$

$$PhNO_2\cdot^- + (AcO)_3Pb\cdot \longrightarrow PhNO_2 + Pb(OAc)_2 + AcO^- \tag{2}$$

$$R^+ + AcO^- \longrightarrow \mathbf{2} \tag{3}$$

as that shown in eq 1–3. Nitrobenzene recoveries were

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(33) C. S. Rondestvedt, Jr., and H. S. Blanchard, *J. Org. Chem.*, **21**, 229 (1956).

(34) The highest migratory ratios obtained with **1c** are much lower than the *p*-methoxyphenyl:phenyl ratios reported for ionic rearrangements in related systems.[14,15] However, a heterolytic mechanism for the present reaction cannot be ruled out on this basis, since the different ratios might simply be due to changes in the nature of the leaving group. Moreover, the possibility that the radical mechanism occurred to an appreciable extent in the high-ratio runs with **1c** cannot be discounted. Even if complete inhibition of a radical chain process (see below) occurred in these cases, significant amounts of rearrangement products still might have been formed from radicals generated in the initiation reaction. The concerted radical mechanism has no well-established analogies; thus there is no firm basis for deciding what the migratory ratio should be for this type of process.

(35) If the migratory ratios for the "pure" radical and quasiionic mechanisms are taken to be 1.1 and 14, respectively, it can readily be shown that only 40% rearrangement occurred *via* the radical mechanism in expt 19. Surprisingly, this value increases only slightly (to 52%) if a quasiionic ratio of 1000 (*cf.* ref 15) is assumed. When the quasiionic mechanism is considered to be homolytic, the radical ratio then refers, of course, only to that fraction of rearrangement which occurs during chain propagation.

(36) D. Benson, L. H. Sutcliffe, and J. Walkley, *J. Am. Chem. Soc.*, **81**, 4488 (1959).

(37) (a) D. H. Hey, M. J. Perkins, and G. H. Williams, *Chem. Ind.* (London), 83 (1963); (b) C. D. Hall, *ibid.*, 384 (1965); (c) G. B. Gill and G. H. Williams, *J. Chem. Soc.*, *Phys. Org. Sect.*, 880 (1966); (d) G. R. Chalfont, D. H. Hey, K. S. Y. Liang, and M. J. Perkins, *Chem. Commun.*, 367 (1967).

(38) R. A. Benkeser and W. Schroeder, *J. Am. Chem. Soc.*, **80**, 3314 (1958).

(39) R. A. Jackson and W. A. Waters, *J. Chem. Soc.*, 1653 (1960).

(40) A. L. Buley and R. O. C. Norman, *Proc. Chem. Soc.*, 225 (1964); W. E. Griffiths, G. F. Longster, J. Myatt, and P. F. Todd, *J. Chem. Soc.*, *Phys. Org. Sect.*, 1130 (1966); A. L. Buley, R. O. C. Norman, and R. J. Pritchett, *ibid.*, 849 (1966); W. E. Griffiths, G. F. Longster, J. Myatt, and P. F. Todd, *ibid.*, 533 (1967).

always considerably less than quantitative, but the significance of this observation is not clear, since large losses may have occurred during work-up operations.[41] Further work to elucidate the mechanism of inhibition by nitrobenzene is clearly required.

Since molecular oxygen is known to be an excellent scavenger for carbon radicals,[42] its failure to affect the yields and migratory ratios of the reactions in Table I (experiments 6, 21, and 33) is surprising and demands an explanation. Low oxygen solubility under the experimental conditions is undoubtedly a contributing factor, but this constitutes only a partial explanation, since oxygen strongly inhibits the lead(IV)-induced oxidative decarboxylation of aliphatic acids at the boiling point of benzene.[7c] Two additional factors may also contribute to the ineffectiveness of oxygen in the present case: (a) slow rates or, more likely, reversibility in the reaction of oxygen with resonance-stabilized bridged radicals (*cf.* 7) and/or $Ar_2\dot{C}OAr$, and (b) very rapid oxidation of these radicals by lead(IV) and lead(III) (here oxidation should be much faster than oxidation of the simple primary and secondary aliphatic carbon radicals generated in the oxygen-inhibited oxidative decarboxylations[7c]). Reversible oxygenation of the triphenylmethyl radical has now been conclusively demonstrated,[43] and there are strong indications for the occurrence of reversibility in the reaction of oxygen with other carbon radicals which are highly stabilized by resonance.[43–45]

A plausible mechanism for the radical chain oxidation of triarylmethanols with lead tetraacetate is summarized in eq 4–9. An analogous scheme which does not include lead(III) intermediates can also be written.[46]

Initiation

$$Ar_3COH + Pb(OAc)_4 \longrightarrow \underset{\mathbf{5}}{Ar_3COPb(OAc)_3} + HOAc \qquad (4)$$

$$\mathbf{5} \longrightarrow Ar_3CO\cdot + (AcO)_3Pb\cdot \qquad (5)$$

Propagation

$$Ar_3CO\cdot \longrightarrow Ar_2\dot{C}OAr \qquad (6)$$

$$Ar_2\dot{C}OAr + \mathbf{5} \longrightarrow \mathbf{2} + \underset{\mathbf{8}}{Ar_3CO\dot{P}b(OAc)_2} \qquad (7)$$

$$\mathbf{8} \longrightarrow Pb(OAc)_2 + Ar_3CO\cdot \qquad (8)$$

Termination

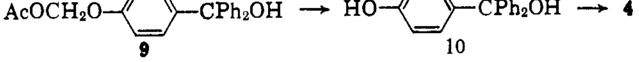
$$Ar_2\dot{C}OAr + (AcO)_3Pb\cdot \longrightarrow \mathbf{2} + Pb(OAc)_2 \qquad (9)$$

The possible involvement of lead(IV) and lead(III) species incorporating more than one triarylmethoxy ligand is neglected for the sake of simplicity, and side reactions such as those involved in the radical chain decomposition of lead tetraacetate itself are also not included. The effects of pyridine and copper salts are expected to parallel the effects observed in oxidative decarboxylations with lead tetraacetate; Kochi's paper[7c] should be consulted for mechanistic details.

An alternative to eq 5 would involve initial formation of **8** from **5**, followed by eq 8. Loss of an acetoxy radical from **8** might be competitive with eq 8, although the lack of evidence for this process was pointed out previously in another connection.[21a] Preferential alkoxy cleavage might be rationalized on the grounds that the bonds between lead and carboxyl oxygen are more ionic in character,[47] thus stronger and less susceptible to homolysis, than the bond between lead and alkoxy oxygen.

Oxidation of chain-carrying carbon radicals by lead(IV) could occur either at the stage indicated by eq 7 or earlier at the (hypothetical) bridged radical stage (*cf.* 7). The detailed mechanism of this oxidation should closely resemble the mechanism of radical oxidation by lead(IV) tetracarboxylates, which apparently occurs predominantly *via* electron transfer rather than ligand transfer.[7c] Preferential transfer of acetoxy (eq 7) rather than triphenylmethoxy is explicable on this basis, since acquisition of an extra electron by **5** should cause it to decompose with loss of the more stable anion (acetate). Acetoxy transfer from **5** is also favored statistically. Triphenylmethoxy transfer might have occurred to some extent, although there was no evidence for the presence of the ketals which would have resulted from this process. These ketals, if present, would have been destroyed during hydrolysis, and their formation obviously would have had no effect on the migratory aptitude measurements.

Formation of the by-product, **4**, in reactions with alcohol **1c** can also be accounted for in terms of a radical mechanism. Of significance in this connection is the fact that yields of **4** were highest (0.10–0.15 mol/mol of **1c**) under conditions where radical-induced decomposition of lead tetraacetate itself is believed to have occurred to the greatest extent (experiments 29, 30, and 37). The large numbers of methyl radicals produced in these runs would have undergone oxidation at a relatively slow rate[7c] and might have survived long enough to abstract hydrogen from the relatively weak CH bonds of the methoxy group. Transfer of an acetoxy ligand to the radical thus formed would give **9**, whose hydrolysis should produce compound **10**. Conversion of **10** to **4** might then have occurred, either during hydrolysis or



9 10

at the high temperatures used for the glpc analyses.[48]

As regards the lead tetraacetate oxidation of triphenylmethanol itself, the relative extents to which the

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(41) For example, glpc analysis of the product from expt 22 showed that only about 11% of the starting nitrobenzene was present after work-up, whereas analysis of the total, unhydrolyzed product obtained from a duplicate experiment showed 61% recovery. In the latter case, there were indications that failure to remove residual lead(IV) may have affected the glpc determination.

(42) For a summary of absolute rate constants, see W. H. Starnes, Jr., *J. Org. Chem.*, 31, 1436 (1966).

(43) E. G. Janzen, F. J. Johnston, and C. L. Ayers, *J. Am. Chem. Soc.*, **89**, 1176 (1967).

(44) G. A. Russell, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, pp 110–111; S. W. Benson, *J. Am. Chem. Soc.*, 87, 972 (1965).

(45) Related studies with other substrates have shown that primary aliphatic carbon radicals generated in the lead tetraacetate–monohydric alcohol reaction can be readily trapped by oxygen (W. H. Starnes, Jr., manuscript in preparation).

(46) The possible involvement of lead(III) species in oxidative decarboxylations with lead tetraacetate has been discussed by Kochi[7c] and is said to be supported by esr measurements (T. W. Bethea and J. K. Kochi, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 12–17, 1965, p 12S). The apparent formation of hexamethyldiplumbane upon thermal decomposition of trimethylplumbane is consistent with the incursion of the radical $(Me)_3Pb\cdot$ as a stable intermediate [R. Duffy, J. Feeney, and A. K. Holliday, *J. Chem. Soc.*, 1144 (1962)]. Recent esr studies have failed to provide evidence for the intermediacy of lead(III) in the oxidative decarboxylation reaction [J. K. Kochi, J. D. Bacha, and T. W. Bethea III, *J. Am. Chem. Soc.*, **89**, 6538 (1967)].

(47) Considerable ionic character is exhibited by the lead–oxygen bonds in lead tetraacetate itself [K. Heusler, H. Labhart, and H. Loeliger, *Tetrahedron Letters*, 2847 (1965)].

(48) *Cf.* K. I. Beynon and S. T. Bowden, *J. Chem. Soc.*, 4247 (1957).

radical and quasiionic mechanisms occur have not yet been established with certainty. However, the fact that this alcohol gave such low yields of benzophenone under conditions which strongly favor the quasiionic mechanism (experiments 9 and 10; compare experiments 31–33) strongly suggests that little, if any, reaction occurred *via* the quasiionic route in the tabulated triphenylmethanol experiments. The low yields of ketone obtained in experiments 9 and 10 also indicate that inhibition of the radical chain mechanism occurs in acetonitrile, or that acetonitrile greatly enhances the rate of the normal termination process (eq 9) relative to propagation (eq 7). This interesting solvent effect merits further investigation. An additional indication for the occurrence of a radical chain mechanism in the oxidation of **1a** is provided by the reduced yields of benzophenone obtained in reactions inhibited by nitrobenzene (experiments 4 and 5), although the reduction observed in experiment 4 is of doubtful significance in view of the rather poor reproducibility of the benzophenone yields obtained in experiments 1–3. The low reproducibility may have been due to the adventitious presence of an inhibiting species or to the partially heterogeneous nature of the reaction; no information regarding this point is available at present.

Mechanism of the Oxidation of Other Alcohols. In view of the results obtained in the present study, the occurrence of radical chain mechanisms during the oxidation of most types of monohydric alcohols with lead tetraacetate seems highly probable. The nature of the chain-carrying carbon radicals involved in a particular reaction will depend, of course, upon the relative rates of the various processes by which these radicals can be formed from the alkoxy radical intermediate. Reactions of alkoxy radicals leading to carbon radicals include hydrogen abstraction, β scission, addition to unsaturated linkages, and rearrangement of an unsaturated group from carbon to oxygen (as in the present work); evidence for occurrence of all of these processes during lead tetracetate–alcohol reactions is available in the literature.[2,4–7]

It is of some interest to note that a chain mechanism incorporating alkoxy radicals and α-hydroxy carbon radicals can also be written for the well-known lead tetraacetate cleavage of glycols,[49] although no direct evidence for operation of such a mechanism can be cited at the present time.

Finally, it must be emphasized that homolytic mechanisms are not necessarily involved in the formation of *all* of the products obtained from monohydric alcohols and lead tetraacetate. Conversion of starting alcohol to the corresponding acetate seems to require the operation of one or more nonradical mechanisms,[6j,o,7b,e,f,50] and carbonyl formation *without* β scission may occur primarily *via* a heterolytic process (especially in the presence of pyridine or polar solvents at relatively low temperatures).[6g,j-l,n,o,22b] In the case of certain unsaturated alcohols, cyclic ether formation may well involve initial attack of the olefinic linkage by cationic lead.[7g] Quasiionic processes such as that encountered in the present work constitute an additional mechanistic possibility, but they are likely to be observed only in special situations where neighboring groups bearing good electron-donor substituents are close to the hydroxyl function. Particularly instructive in this regard is the failure of alcohol **1b** to react *via* the quasiionic path, even though radical chain oxidation of this compound was probably inhibited strongly by the nitrophenyl group. The relatively low yields of rearrangement products obtained from the nitro alcohol can be taken as direct evidence for an autoinhibition process.[51]

Experimental Section[52]

Materials. Lead tetraacetate (Matheson) was dried in a vacuum desiccator over sodium hydroxide. Anhydrous calcium carbonate (Matheson, ACS reagent) was kept in a vacuum oven at 60° under 5–10 mm pressure. Benzene (Baker reagent grade) was dried over sodium wire; acetonitrile (Eastman) was distilled from calcium hydride in a dry atmosphere. Nitrobenzene (Eastman) was washed in succession with 10% sulfuric acid, water, 10% sodium hydroxide, and water, then dried and distilled. Literature procedures were used to prepare pure reference samples of methoxyphenoxydiphenylmethane,[53] diphenoxydiphenylmethane,[54] and 4-diphenylmethylene-2,5-cyclohexadien-1-one (**4**);[55] structures of the products were verified by the usual variety of spectroscopic methods. All of the other chemicals used were highly purified commercial materials. Purities were checked by spectral measurements, determinations of various physical constants, and, where possible, glpc analysis.

Instrumental Analyses. Infrared spectra of pure compounds were obtained with a Perkin-Elmer instrument, Model 21; those of crude mixtures were usually recorded with a Perkin-Elmer Infracord. Nmr measurements were made at 100 Mc with a Varian Associates instrument, Model HA-100; dilute solutions containing tetramethylsilane for internal standardization were employed. Chemical ionization mass spectra[9] were obtained with the Esso chemical physics mass spectrometer using methane as the reactant gas. Conventional mass spectra were recorded with a CEC instrument, Type 21-103C, or with an AEI MS-9 high-resolution spectrometer. Programmed-temperature glpc analyses were performed with an F & M instrument, Model 500, which was equipped with the following columns: A, stainless steel, 6 ft × 0.25 in. (o.d.), packed with SE-30 (15%) on Chromosorb W (45–60 mesh); B, stainless steel, 2 ft × 0.25 in. (o.d.), packed with SE-30 (0.5%) on Chromosorb P (40–60 mesh). Helium was used as the carrier gas; column temperature was raised at the rate of 8°/min from 100 to 350° (column A) or from 75 to 350° (column B). Peak areas were measured with the aid of a planimeter; sensitivity factors were determined with known mixtures of pure reference compounds.

Diphenyl-*p*-nitrophenylmethanol (1b). A solution of diphenyl-*p*-nitrophenylbromomethane[56] (20.00 g) in acetone (200 ml) was combined with water (75 ml) and allowed to stand at room temperature for 3 days. The acetone was then evaporated, and the product was recovered by extracting with ether. The extracts were washed in succession with 3 *N* sodium carbonate and saturated sodium chloride solution, dried, and evaporated. Recrystallization of the residue from cyclohexane afforded 14.53 g (88%) of **1b**, mp 97–100°. A further recrystallization from the same solvent gave 9.85 g (59%) of material which melted at 98–100° (lit.[57] mp 97.5–98.5°) and contained no impurities detectable by nmr or glpc analy-

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(49) For a recent review of this reaction, see C. A. Bunton, "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, p 398 ff.

(50) M. L. Mihailović, R. I. Mamuzić, L. Žigić-Mamuzić, J. Bošnjak, and Ž. Čeković, *Tetrahedron*, 23, 215 (1967).

(51) Reduction in the rate of formation of **5**, owing to the decreased nucleophilicity of the hydroxyl group, might also have tended to lower the over-all rate of reaction of the nitro alcohol.

(52) Melting points were determined with a Fisher-Johns apparatus and are uncorrected. Elemental microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Organic solutions were dried with Drierite unless noted otherwise. Evaporations were done at ambient temperature under 5–10 mm pressure on Rinco rotary evaporators. 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.

(53) A. B. Bořkovec, *J. Org. Chem.*, 26, 4866 (1961).

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sis. This preparation of **1b** is similar to that described by Saunders and Ware.[57]

Diphenyl-*p*-methoxyphenylmethanol (1c). Crude **1c**, obtained from the reaction of phenylmagnesium bromide with methyl anisate,[58] was converted to the corresponding chloride in the manner described by Gomberg and Buchler.[59] Hydrolysis of 30.00 g of purified chloride according to the method described above for **1b** gave an essentially quantitative yield of the desired alcohol, mp 79.5–81° before recrystallization. A single recrystallization from cyclohexane yielded 26.10 g (92%) of product, mp 81–81.5° (lit.[57,58] mp 84°), which was shown to be entirely homogeneous by glpc analysis and nmr measurements.

Dimethoxyphenyl-*p*-methoxyphenylmethane (*p*-Methoxybenzophenone Dimethyl Ketal). A well-stirred mixture of *p*-methoxybenzophenone (10.6 g, 0.0499 mol) and phosphorus pentachloride (11.1 g, 0.0533 mol) was kept at 62–64° under nitrogen for 17 hr. After cooling to room temperature, the entire mixture was taken up in 300 ml of anhydrous ether and washed as quickly as possible with two 100-ml portions of ice water. Drying over calcium chloride, followed by evaporation of the ether, afforded a solid whose infrared spectrum showed none of the strong bands associated with the starting ketone. The solid (presumed to be mostly dichlorophenyl-*p*-methoxyphenylmethane)[60] was redissolved in dry ether (200 ml), and the solution was added slowly (10–15 min) with stirring to a cloudy solution of sodium methoxide (27.0 g, 0.500 mol) in methanol (reagent grade, 750 ml). After having been stirred for an additional 30 min and then allowed to stand for 2 hr, the mixture was evaporated to a volume of approximately 100 ml, mixed with 400 ml of water, and extracted with three 100-ml portions of ether. The extracts were washed with three 50-ml portions of water, dried over potassium carbonate, and evaporated. Recrystallization of the residue from reagent grade methanol (to which a small amount of sodium methoxide was added) gave 7.02 g (54%) of the desired ketal as flat, colorless needles, mp 83.5–84.5° (not raised by further recrystallizations). This product contained no impurities that were detectable by glpc analysis, and its infrared spectrum showed no carbonyl absorption. The nmr spectrum (CCl_4) exhibited singlets at τ 6.98 (6 H, methoxyls of ketal function) and 6.31 (3 H, nuclear methoxyl), a skewed doublet intermixed with additional small peaks at τ 3.23–3.40 (2 H, upfield branch of aromatic A_2B_2 pattern), and a complex multiplet at τ 2.53–2.97 (7 H, the remaining aromatic protons). Hydrolytic decomposition of this very sensitive ketal was prevented by storing the compound in a desiccator over potassium hydroxide.

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.50; H, 7.13.

Reactions of Triarylmethanols with Lead Tetraacetate. All reactions (Table I) were run in thermostated flasks equipped with an efficient magnetic stirrer, a reflux condenser, an assembly permitting blanketing with the desired gas, and (in many cases) a mercury-filled gas buret. Experiments with pure oxygen were performed under a slow, continuous gas sweep in order to remove evolved carbon dioxide and avoid dilution of the gaseous atmosphere. In other experiments volumetric measurement of the rate of gas evolution provided a rough measure of the over-all rate of disappearance of lead(IV). Calcium carbonate was added solely for the purpose of scavenging acetic acid and is presumed to have had no other effect on these reactions. Lead(IV) conversions were estimated qualitatively from the amounts of PbO_2 that precipitated upon addition of water during the work-up procedure (see below). These conversions were essentially complete in experiments 6–10, 13, 14, 16, 17, 24–31, 34, and 37; approximately 80–90% complete in experiments 1–3, 15, 18–21, 32, 33, 35, and 36; and considerably less than complete in experiments 4, 5, 11, 12, 22, and 23. After cooling, the reaction mixtures were filtered, and the recovered solids were washed several times on the filter with fresh portions of solvent. In a few runs these solids were thoroughly dried and shown to contain no aromatic constituents by qualitative infrared analysis (aromatic CH out-of-plane bending bands were absent). The combined filtrate and washings were thoroughly mixed with an excess of water and filtered to remove PbO_2, which was washed repeatedly on the filter with benzene and with water. (In runs using acetonitrile as solvent, the original organic filtrate was evaporated under vacuum and the residue taken up in benzene prior to addition of water.) The two layers of the combined filtrate and washings were separated, and solvent was removed from the organic moiety by evaporation. Hydrolysis of the residue was effected by allowing it to stand for at least 2–3 days at room temperature in a solution of concentrated hydrochloric acid (1 ml), tetrahydrofuran (35 ml), and water (4 ml), or in a solution of potassium hydroxide (1.8 g, *ca.* 10 mol/mol of starting alcohol) in methanol (23.5 ml) and water (1.5 ml). In some runs (*cf.* Table I) basic hydrolysis was carried out at reflux temperature. Following evaporation of the organic solvent, the hydrolysate was partitioned between ether and 5% aqueous sodium hydroxide, and the ether phase was thoroughly extracted with fresh portions of the caustic solution, dried, and evaporated to give a residue (fraction A) which was analyzed quantitatively by programmed-temperature glpc (column A) after addition of a weighed amount of an appropriate internal standard. Infrared examination of the A fractions showed that complete hydrolysis of the hemiketal acetates had occurred under all of the conditions employed. The caustic extracts were combined with the original aqueous filtrate and washings, adjusted to pH 2 with concentrated hydrochloric acid, and extracted completely with ether over a period of several days in a continuous extraction apparatus. The ether solution was dried and evaporated, and the residual mixture of acidic hydrolysis products (fraction B) was analyzed by programmed-temperature glpc using the internal standard method. Acetic acid was detected qualitatively in these mixtures (by retention time) but was not determined quantitatively. The B fractions from experiments with alcohol **1a** or **1c** were analyzed on column A; column B was used for B fractions from alcohol **1b**. All products except **3** (see below) were identified by comparing their retention times and the infrared, nmr, and mass spectra of trapped glpc peaks with those of authentic specimens. In order to check the accuracy of the method of analysis, several standard mixtures containing starting alcohol and all of the hydrolysis products of the corresponding hemiketal acetate(s) were subjected to the various procedures used for hydrolysis, worked up in the manner described above, and analyzed in the usual way. On the basis of the results, the maximum error in relative migratory aptitudes calculated from the yields of ketones and ketals was estimated to be ±8% of the values obtained.

The infrared spectrum of the trapped peak containing compound **3** showed no OH or carbonyl absorption. The mass spectrum (60 eV) showed only a weak parent peak at *m/e* 304 but displayed strong peaks at *m/e* 274.1350, 273.1282, 260.1189, and 258.1061 (calcd for $C_{20}H_{18}O$, $C_{20}H_{17}O$, $C_{19}H_{16}O$, and $C_{19}H_{14}O$: *m/e* 274.1357, 273.1279, 260.1201, and 258.1044, respectively). Signals appeared in the nmr spectrum (CS_2) of the compound at τ 7.07 (singlet, 3 H, aliphatic methoxyl), 6.29 (singlet, 3 H, aromatic methoxyl), 3.29–3.39 (distorted doublet, 2 H, upfield branch of aromatic A_2B_2 pattern), and 2.64–2.97 (complex multiplet, 12 H, aromatic protons), confirming the structure assigned.

In a number of preliminary experiments (reaction times <24 hr) the infrared spectra of the total, unhydrolyzed product fractions [examined after removal of lead(IV)] showed no benzophenone carbonyl absorption(s) but invariably displayed a strong band (or bands) assignable to the ester carbonyl(s) of the hemiketal acetate(s). Exposure of these mixtures to the laboratory air led to the gradual appearance of benzophenone absorption and caused concomitant decreases in the ester bands. Attempts to isolate compound **2a** from some of the mixtures by crystallization, solvent extraction, or column chromatography gave incomplete separation from the starting alcohol and usually led to partial or complete hydrolysis.

Upon crystallization from aqueous methanol, the total, unhydrolyzed product obtained from a run similar to experiments 1–3 (reaction time, 102 hr) afforded methoxyphenoxydiphenylmethane, mp 115–117° (lit.[53] mp 117.5°), in *ca.* 15% yield. The structure of the compound was confirmed by a mixture melting point determination and by spectral comparisons with authentic material.[53]

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