Reactions of Lead Tetra-acetate. Part XIII.[1] Homolytic and Heterolytic Mechanisms in the Oxidation of Alcohols

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The products formed during the oxidation of $PhCH_2{\cdot}CPhAr{\cdot}OH$, $Me_3C{\cdot}CPhAr{\cdot}OH$ (Ar = Ph or *p*-anisyl), $AnCH_2{\cdot}CPh_2{\cdot}OH$, $PhCH_2{\cdot}CHAn{\cdot}OH$, and $Me_3C{\cdot}CHAn{\cdot}OH$ (An = *p*-anisyl) by lead tetra-acetate in various solvents have been determined. For the tertiary alcohols, it is argued that the t-butyl-alcohols react essentially completely by a heterolytic mechanism in which the t-butylcarbonium ion departs from an alkoxy-lead(IV) derivative, whereas the benzyl alcohols react predominantly by a homolytic mechanism in which the benzyl (or 4-methoxybenzyl) radical is formed. For the secondary alcohols, the heterolytic and homolytic fragmentations are competitive with simple oxidation to the corresponding ketone.

WE have previously shown that the triarylmethanols, $ArPh_2C{\cdot}OH$ (Ar = Ph or *p*-anisyl), undergo oxidative rearrangement when heated with lead tetra-acetate in acetonitrile, acetic acid, or benzene; evidence was adduced that reaction in the first two solvents occurs predominantly through the heterolysis of the O–Pb bond of an alkoxy-lead derivative, whereas in benzene the predominant pathway involves homolysis of this bond.[1] In order to gain further understanding of the factors which control the relative importance of the heterolytic and homolytic routes for such alkoxy-lead(IV) derivatives, we have now studied the behaviour of a variety of alcohols of the general type $PhR^1R^2C{\cdot}OH$ (R^1 = Ph, *p*-anisyl, or H; R^2 = benzyl, 4-methoxybenzyl, or t-butyl) when oxidised with lead tetra-acetate in various solvents.

The general method consisted of heating a solution of the alcohol and a small excess of lead tetra-acetate at constant temperature until the lead(IV) had been completely destroyed. The solution was poured into water and the ether extract was washed with 5M-hydrochloric acid to ensure the complete hydrolysis of acetal-type products (cf. ref. 1). Wherever possible, the products were isolated by preparative g.l.c. and identified by comparison with authentic materials; where they were present in very small yield they were identified by comparison of their retention times with those of authentic materials on at least two g.l.c. columns. Quantitative analysis was by analytical g.l.c., the yields being reproducible to within ±3%. The results are in Tables 1—8.

TABLE 1

Distribution of products, and reaction times, for the oxidation of 1,1,2-triphenylethanol

Solvent	MeCN	HOAc	PhH	CCl_4	$PhH{-}CCl_4$ (1 : 1)	$PhH{-}CCl_4$ (10 : 1)
Reaction time (hr.):	36	50	50	220	120	100
Products (%):						
PhCHO	2·4	3·8	2·9			
$PhCH_2Cl$				24·9	30·1	9·7
$PhCH_2{\cdot}OAc$...	17·7	4·8	32·6	22·9	23·9	27·8
$PhCH_2Ph$ ...			1·6		Trace	1·2
$PhCH_2{\cdot}CH_2Ph$	0·2	0·1	5·2		Trace	2·5
Ph_2CO	47·7	13·3	52·8	74·3	72·6	55·3

The chief product from the tertiary alcohols is invariably a ketone formed by fragmentation of the benzyl or t-butyl substituent. However, there are clear indications of variations of the mechanism of the reaction with structure as well as [1] with solvent; the variations are revealed by comparison of the behaviour of the

TABLE 2

Distribution of products for the oxidation of 1,1,2-triphenylethanol in benzene *

	Ratio of $[Pb(OAc)_4]$: $[PhCH_2{\cdot}CPh_2{\cdot}OH]$ 1 : 1	1 : 2	1 : 5
Product:			
PhCHO	2·9	2·4	1·0
$PhCH_2{\cdot}OAc$	32·6	43·4	13·0
$PhCH_2Ph$	1·6	2·8	5·5
$PhCH_2{\cdot}CH_2Ph$ ...	5·2	13·4	19·5
Ph_2CO	52·8	67·2	63·5

* Yields are expressed as (moles product/moles oxidant) ×100%.

TABLE 3

Distribution of products, and reaction times, for the oxidation of 1-*p*-anisyl-1,2-diphenylethanol

Solvent		MeCN	PhH
Reaction time (hr.)	....	9	50
Products (%):	PhCHO	3·8	3·4
	$PhCH_2{\cdot}OAc$	8·5	23·3
	p-$MeO{\cdot}C_6H_4{\cdot}OAc$	6·2	
	p-$MeO{\cdot}C_6H_4{\cdot}OH$	1·0	
	$PhCH_2Ph$		2·6
	$PhCH_2{\cdot}CH_2Ph$	0·2	8·6
	$PhCO{\cdot}CH_2Ph$	11·6	
	p-$MeO{\cdot}C_6H_4{\cdot}COPh$	30·2	37·2

TABLE 4

Distribution of products, and reaction times, for the oxidation of t-butyldiphenylmethanol

Solvent		HOAc	PhH
Reaction time (hr.)	....	1	1·2
Products (%):	$Bu^t{\cdot}CPh_2OH$	30·8	27·0
	Ph_2CO	69·2	73·0
	$Me_2C{=}CH_2$	0·9	22·2
	Bu^tOAc	29·4	17·0

TABLE 5

Distribution of products, and reaction times, for the oxidation of *p*-anisyl-t-butylphenylmethanol

Solvent		HOAc	PhH
Reaction time (hr.)	....	0·5	0·7
Products (%):	*p*-$MeO{\cdot}C_6H_4{\cdot}COPh$	73·3	85
	$Me_2C{=}CH_2$	0·9	17·6
	Bu^tOAc	18·5	7·5

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[1] Part XII, R. O. C. Norman and R. A. Watson, *J. Chem. Soc.* (*B*), 1968, 184.

TABLE 6

Distribution of products, and reaction times, for the oxidation of 2-*p*-anisyl-1,1-diphenylethanol

Solvent	MeCN	HOAc	PhH	CCl_4
Reaction time (hr.)	2·7	3	5	24
Products (%):				
p-$MeO\cdot C_6H_4\cdot CHO$	Trace	12·0	Trace	
p-$MeO\cdot C_6H_4\cdot CH_2\cdot OAc$	86·8	53·7	66·7	44·1
p-$MeO\cdot C_6H_4\cdot CH_2Cl$				18·5
Ph_2CO	96·6	66·8	62·4	64·7

TABLE 7

Distribution of products, and reaction times, for the oxidation of 1-*p*-anisyl-2-phenylethanol

Solvent	MeCN	PhH	PhH–C_5H_5N
Reaction time (hr.)	4	17	0·25
Products (%):			
PhCHO	3·0	0·7	3·1
$PhCH_2\cdot CHO$	2·8		
$PhCH_2\cdot OAc$	25·6	14·6	0·9
p-$MeO\cdot C_6H_4\cdot CHO$	36·5	16·0	4·7
p-$MeO\cdot C_6H_4\cdot OAc$	1·6		
p-$MeO\cdot C_6H_4\cdot OH$	3·0		
$PhCH_2Ph$		0·3	
$PhCH_2\cdot CH_2Ph$		0·9	
p-$MeO\cdot C_6H_4\cdot CO\cdot CH_2Ph$	28·7	16·3	56·1

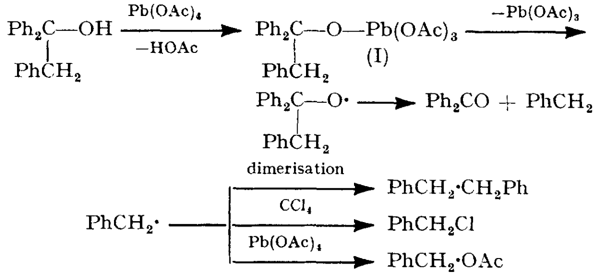
TABLE 8

Distribution of products, and reaction times, for the oxidation of *p*-anisyl-t-butylmethanol

Solvent		HOAc	PhH
Reaction time (hr.)		0·5	0·5
Products (%):	$Bu^tCH(OH)\cdot C_6H_4\cdot OMe$-*p*	32·5	19·2
	p-$MeO\cdot C_6H_4\cdot CHO$	60·3	74·4
	p-$MeO\cdot C_6H_4\cdot COBu^t$	7·2	6·4
	$Me_2C{=}CH_2$		6·0

compounds $PhCH_2\cdot CPh_2\cdot OH$ and $PhCH_2\cdot CPhAn\cdot OH$ with that of $Me_3C\cdot CPh_2\cdot OH$ and $Me_3C\cdot CPhAn\cdot OH$ (An = *p*-anisyl throughout).

That the oxidation of $PhCH_2\cdot CPh_2\cdot OH$ occurs at least in part by a free-radical mechanism is indicated by the formation of bibenzyl and, for reactions with carbon tetrachloride as solvent or co-solvent, of benzyl chloride (Table 1); further, there was g.l.c. evidence for the formation of hexachloroethane in carbon tetrachloride. We conclude that the benzyl radical is formed by fragmentation, as in Scheme 1. Apart from its giving bibenzyl and benzyl chloride, it is probable that it forms benzyl acetate *via* its oxidation by lead(IV) to the benzyl carbonium ion;[1,2] the lower yield of benzyl acetate (and of bibenzyl) in carbon tetrachloride than in benzene (in which the overall yield is significantly greater) then follows because the benzyl radical is in part removed by reaction with the solvent instead of undergoing oxidation (or dimerising). Diphenylmethane can be formed in benzene by reaction of the benzyl radical with the solvent.[3]



SCHEME 1

As the concentration of the alcohol is increased, the rate of generation of the benzyl radical should be higher and the probability of its dimerising instead of being oxidised should be enhanced. The data in Table 2 show that this expectation is borne out.

There is no evidence for the concurrence of a heterolytic oxidation of $PhCH_2\cdot CPh_2\cdot OH$. If the O–Pb bond in the alkoxy-lead(IV) derivative (I) were to undergo heterolysis, we should expect the migration of a phenyl group from carbon to oxygen to occur at least as readily as the alternative migration of the benzyl group, since phenyl has a very much greater migratory aptitude than benzyl in the solvolytic rearrangement of 1-R-1-methylethyl *p*-nitroperbenzoates (R = Ph or benzyl);[4] this would lead to the formation[1] of deoxybenzoin, but none was detected. The absence of an ionic rearrangement is notable because there is a significant degree of phenyl migration during the oxidation of *p*-anisyldiphenylmethanol by lead tetra-acetate, and oxidation is faster, for a given solvent, than for $PhCH_2\cdot CPh_2\cdot OH$.[1] This comparison shows the importance of the aryl groups in stabilising the carbon radical $PhAn\dot{C}{-}OPh$ or the carbonium ion $PhAn\overset{+}{C}{-}OPh$ which result from the homolytic or heterolytic rearrangements, respectively,[1] in the decomposition of the lead(IV) complex formed by $Ph_2AnC\cdot OH$.

The oxidation of $PhCH_2\cdot CPhAn\cdot OH$ in benzene occurs at about the same rate as that of $PhCH_2\cdot CPh_2\cdot OH$, and gives bibenzyl but no deoxybenzoin or 4-methoxydeoxybenzoin. We conclude that the free-radical mechanism corresponding to that in Scheme 1 constitutes the predominant pathway. However, oxidation in acetonitrile is considerably faster for the *p*-methoxy-compound than for the unsubstituted alcohol, the yield of bibenzyl is very small, and the products include deoxybenzoin, *p*-methoxyphenol, and 4-acetoxyanisole, indicating[1] the occurrence of a 1,2-migration of the *p*-anisyl group to oxygen. The absence of products characteristic of the migration of the phenyl group (*e.g.* 4-methoxydeoxybenzoin), of which $<0.5\%$ would have been detected, indicates a migratory aptitude of *p*-anisyl relative to phenyl of at least 20 : 1, so that we conclude, by analogy with our previous discussion,[1] that the heterolytic rearrangement in Scheme 2 occurs concurrently with the free-radical reaction in acetonitrile.

In contrast to the behaviour of $PhCH_2\cdot CPh_2\cdot OH$, that

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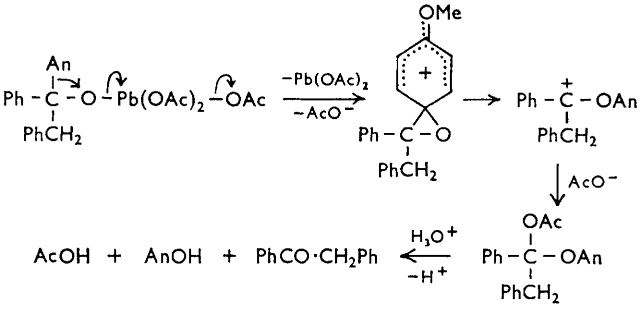
[2] J. K. Kochi, *Science*, 1967, **155**, 415.

[3] F. D. Greene, H. P. Stein, C.-C. Chu, and F. M. Vane, *J. Amer. Chem. Soc.*, 1964, **86**, 2080.

[4] E. Hedaya and S. Winstein, *J. Amer. Chem. Soc.*, 1967, **89**, 1661.

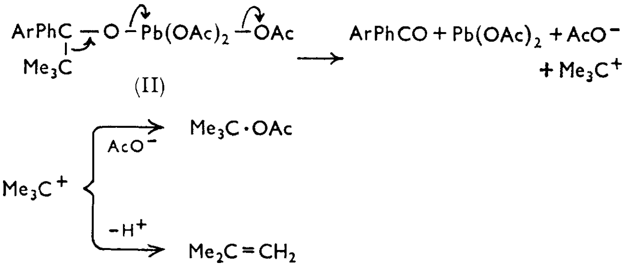
of $Bu^tCPh_2{\cdot}OH$ (Table 4) shows none of the characteristics of a free-radical reaction. In particular, first, the latter alcohol is oxidised considerably faster than the former [although, on steric grounds, we should expect the concentration of alkoxy-lead(IV) derivatives to be smaller for the t-butyl alcohol], whereas $PhCH_2$–C bonds are weaker than Bu^t–C bonds by about 15 kcal./mole [5] and should undergo homolysis faster. Secondly, hexamethylethane could not be detected amongst the products, although this has been identified as a product of the t-butyl radical in another reaction.[6] However, the results are consistent with the loss of the t-butyl carbonium ion from an alkoxy-lead(IV) derivative, as in Scheme 3 (Ar = Ph); the greater rate for the t-butyl than for the benzyl alcohol is to be expected by analogy with the findings that t-butyl chloride is *ca.* 360 times as reactive as benzyl chloride in S_N1 solvolysis in 70% aqueous acetone [7] and that, in the solvolysis of 1-R-1-methylethyl *p*-nitroperbenzoates, the compound R = Bu^t is more than 100 times as reactive as the compound R = benzyl.[4] We reject the alternative ionic mechanism, in which the t-butyl group migrates to oxygen synchronously with heterolysis of the O–Pb bond, for the following reason. If this process were to occur, we should expect the formation of the ketal-type product, $Ph_2C(OBu^t)(OAc)$, from which benzophenone would not be completely released until acidic hydrolysis. However, in contrast to our findings in those cases in which an aryl group migrates to oxygen, both previously [1] and in the present work, the measured yield of the ketone was not increased by acid hydrolysis, either in this case or for Ar = *p*-anisyl. Moreover, the n.m.r. spectrum of the reaction mixture after hydrolysis did not contain the resonance at τ 8·8 characteristic of t-butanol whose formation would be expected on hydrolysis of $Ph_2C(OBu^t)(OAc)$.



SCHEME 2

The introduction of a *p*-methoxy-substituent into t-butyldiphenylmethanol caused an increase in the rate of oxidation and no unchanged alcohol was recovered (compare Tables 4 and 5). No pivalophenone was detected, so that the extent of rearrangement of *p*-anisyl from carbon to oxygen is evidently negligible. The increased rate would, however, follow from the fact that the carbonyl group which is partially formed at the transition state for fragmentation of the intermediate (II; Ar = *p*-anisyl) is stabilised by conjugation with the methoxy-substituent.

The formation of 4-methoxybenzyl chloride shows that the oxidation of $AnCH_2{\cdot}CPh_2{\cdot}OH$ in carbon tetrachloride is at least in part homolytic. 4-Methoxydeoxybenzoin was not detected as a product in any solvent, so that there is no indication of the occurrence of a heterolytic rearrangement. However, oxidation is very much faster, for a given solvent, than for $PhCH_2{\cdot}CPh_2{\cdot}OH$, possibly because the radical, *p*-$MeO{\cdot}C_6H_4{\cdot}CH_2{\cdot}$, is stabilised by the methoxy-substituent and so fragments more readily than benzyl. No 4,4′-dimethoxybibenzyl could be detected, but this may be because of the ready oxidation of this compound at a methylene group; *p*-methoxytoluene is significantly more rapidly oxidised by lead tetra-acetate than is toluene.[8]



SCHEME 3

A comparison of the behaviour of the two secondary alcohols, $PhCH_2{\cdot}CHAn{\cdot}OH$ and $Me_3C{\cdot}CHAn{\cdot}OH$, also reveals the marked change which occurs when the t-butyl group replaces the benzyl group (Tables 7 and 8). For both, simple oxidation to the corresponding ketone is competitive with fragmentation. With the benzyl alcohol, the oxidation and the fragmentation of a benzyl group occur to approximately equal extents in acetonitrile and benzene, giving 4-methoxydeoxybenzoin and *p*-anisaldehyde respectively. In acetonitrile, a small proportion of the alcohol is oxidised with 1,2-migration of the *p*-anisyl group, giving phenylacetaldehyde and *p*-methoxyphenol. The inclusion of pyridine in the benzene solution reduces the reaction time and diverts the reaction in favour of the simple oxidation, as expected.[9] With the t-butyl alcohol, on the other hand, the fragmentation of the t-butyl group occurs far more readily than the simple oxidation, and this difference, together with the absence of hexamethylethane and the much greater rate of reaction in benzene of the t-butyl compared with the benzyl alcohol, reinforces our conclusion above that the t-butyl group fragments as the carbonium ion.

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[5] A. F. Trotman-Dickenson, 'Gas Kinetics,' Butterworths, London, 1955, pp. 11—15.

[6] R. N. Birrell and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1960, 4218.

[7] A. Streitwieser, jun., *Chem. Rev.*, 1956, **56**, 571.

[8] G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.*, 1954, 3943.

[9] R. Partch, *Tetrahedron Letters*, 1964, 3071; R. Partch and J. Monthony, *ibid.*, 1967, 4427.

EXPERIMENTAL

^{1}H n.m.r. spectra were measured in solution on a Perkin-Elmer R10 60 Mc./sec. spectrometer, and i.r. spectra were recorded for solutions in chloroform on a Unicam SP 200 spectrophotometer. Analytical g.l.c. was on a Pye instrument (series 104, model 24), with a flame-ionisation detector which was linear over a wide range; the relationship between the quantity of each material and the peak-area it produced was established by the analysis of synthetic mixtures. Two 5-ft. glass columns were used, one containing 10% silicone oil and the other 10% Carbowax 20M, each coated on 60—100 mesh acid-washed Embacel; the former was used for quantitative analysis. Preparative g.l.c. was on an F and M Prepmaster Junior, model 776, with an 8 ft. × $\frac{3}{4}$ in. stainless steel column packed with 20% silicone oil. M.p.s were determined on a Kofler microstage.

Lead tetra-acetate (B.D.H. laboratory reagent) was recrystallised from acetic acid and filtered under suction. For reactions in acetic acid, the reagent was used directly, but for use in other solvents it was stored in a vacuum-desiccator (P_2O_5 and KOH) for 24 hr. before use. Reactions in acetic acid were at 80° and those in other solvents were at the reflux temperature. For solvents other than acetic acid, calcium carbonate (1·2 mol.) was added to the reaction mixture.

1,1,2-Triphenylethanol was prepared (72%) from benzylmagnesium chloride and benzophenone and had m.p. 89—90° [from benzene–light petroleum (b.p. 60—80°)] (lit.,[10] 89—90°). 1-*p*-Anisyl-1,2-diphenylethanol was prepared (81%) from benzylmagnesium chloride and 4-methoxybenzophenone and had m.p. 110—111° (from ethanol) (lit.,[11] 110·5°). 1-*p*-Anisyl-2-phenylethanol, from benzylmagnesium chloride and *p*-anisaldehyde, had m.p. 59—60° [from light petroleum (b.p. 60—80°)] (lit.,[12] 60—61°). *p*-Anisyl-t-butylphenylmethanol was prepared by treating *p*-anisyl t-butyl ketone (from pivaloyl chloride and anisole [13]) with phenylmagnesium bromide and had m.p. 73—74° (lit.,[14] 67—68°). t-Butyldiphenylmethanol, from benzophenone and t-butylmagnesium chloride,[15] was purified by fractional distillation and had b.p. 188—190°/13 mm., n_D^{21} 1·5748 (lit.,[16] b.p. 148—150°/2·5 mm., n_D^{20} 1·5748); n.m.r. spectrum ($CDCl_3$): aromatic multiplet (10H) at τ 2·3—2·9, singlet (1H) at τ 7·71 (OH), and singlet (9H) at τ 8·87 (CMe_3). α-t-Butyl-4-methoxybenzyl alcohol,[17] from anisaldehyde and t-butylmagnesium chloride, had m.p. 40—41° [from light petroleum (b.p. 40—60°)] (lit.,[17] 41—42°).

2-p-*Anisyl*-1,1-*diphenylethanol*.—The Grignard reagent [18] from *p*-anisyl chloride (from *p*-anisyl alcohol by Newman's method; [19] b.p. 109—113°/13 mm.) (12·5 g.) in ether (150 ml.) was treated with benzophenone (14 g.) in ether (50 ml.). After 1 hr. at the reflux temperature, the mixture was poured when cold into ice-cold dilute hydrochloric acid. The ether layer and further ether extracts were washed with sodium hydrogen carbonate solution and water and dried ($MgSO_4$). After distillation of the solvent, a crude solid (21 g.) crystallised from ethyl acetate. It was treated with ether to remove 4,4′-dimethoxybibenzyl (whose presence was indicated by the n.m.r. spectrum), and recrystallised twice from ethyl acetate to give 2-p-*anisyl*-1,1-*diphenylethanol* (12 g., 49%), m.p. 141·5—143°; n.m.r. spectrum ($CDCl_3$): aromatic resonances (14H) at τ 2·4—3·2, singlet (3H) at τ 6·23 (OMe), singlet (2H) at τ 6·36 (CH_2), and singlet (1H) at τ 7·62 (OH) (Found: C, 82·7; H, 6·4. $C_{21}H_{20}O_2$ requires C, 82·7; H, 6·6%).

Oxidations.—Each alcohol was heated with lead tetra-acetate in the appropriate solvent (20 ml.), and the course of the reaction was followed by periodically withdrawing one drop of the solution and testing with starch–iodide paper. When the reaction was complete, the mixture was poured into water and the ether extract was washed with 5M-hydrochloric acid, sodium hydrogen carbonate solution, and water, and dried ($MgSO_4$). After distillation of the solvent, the mixture was submitted to analytical and separatory techniques. Reaction of $AnCH_2{\cdot}CPh_2{\cdot}OH$ (An = *p*-anisyl) in acetonitrile gave a very small amount of an unidentified material (which was not $AnCH_2{\cdot}NHAc$), and likewise reactions in acetonitrile of $PhCH_2{\cdot}CPh_2{\cdot}OH$, $PhCH_2{\cdot}CPhAn{\cdot}OH$, or $PhCH_2{\cdot}CHAn{\cdot}OH$ gave a small amount of an unidentified material (which was not $PhCH_2{\cdot}NHAc$).

(a) 1,1,2-*Triphenylethanol*. The alcohol (1·37 g.) was treated with lead tetra-acetate (2·28 g.). From the reaction in benzene, benzyl acetate, diphenylmethane, bibenzyl, and benzophenone were isolated by preparative g.l.c. (silicone oil, 200°) and their identities were confirmed by comparison of their n.m.r. and i.r. spectra with those of authentic samples. Benzyl chloride was likewise isolated and identified from the reaction in carbon tetrachloride. The presence of benzaldehyde was inferred from its retention times on two columns, and a small peak with a retention time equal to that of hexachloroethane was observed when carbon tetrachloride was the solvent. Quantitative g.l.c. was at 180° with 4-acetoxyanisole as standard.

Experiments in benzene were also carried out with a two-fold and a five-fold excess of the alcohol over lead tetra-acetate.

(b) 1-p-*Anisyl*-1,2-*diphenylethanol*. The alcohol (1·52 g.) was treated with lead tetra-acetate (2·28 g.). Benzyl acetate, bibenzyl, deoxybenzoin, and (from reaction in acetonitrile) 4-acetoxyanisole were isolated by preparative g.l.c. and were identified by their n.m.r. and i.r. spectra as above. 4-Methoxybenzophenone crystallised from the mother-liquors from the reaction in benzene and was identified by m.p., mixed m.p., and n.m.r. and i.r. spectra. Benzaldehyde, *p*-methoxyphenol, and diphenylmethane were identified by their retention times on two columns. Quantitative g.l.c. was at 180° with benzophenone as standard.

(c) p-*Anisyl-t-butylphenylmethanol*. The alcohol (1·35 g.) was treated with lead tetra-acetate (2·28 g.). During the reaction, volatile products were passed into a cold trap containing a solution of bromine in carbon tetrachloride. The bromine solution was then washed with sodium thiosulphate solution, sodium hydrogen carbonate

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[10] I. Heilbron and H. M. Bunbury, 'Dictionary of Organic Compounds,' 4th edn., Eyre and Spottiswoode, London, 1965.

[11] Beilstein's Handbuch, band VI, 2nd Supplement, 1944, p. 1016.

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solution, and water, and dried ($CaCl_2$). The solution was concentrated, and g.l.c. (silicone oil, 100°) showed the presence of 1,2-dibromo-2-methylpropane, confirmed by its n.m.r. spectrum [20] (CCl_4): singlet (6H) at τ 8·10 and singlet (2H) at τ 6·12; the material was estimated by g.l.c. at 100° with 1,3-dibromopropane as standard. Work-up of the reaction product in the usual way led to the isolation of 4-methoxybenzophenone, identified by m.p. and mixed m.p. with an authentic sample, whose yield was measured by g.l.c. (silicone oil, 180°) with benzophenone as standard. In some experiments, the reaction mixture was extracted with methylene dichloride and, after removal of the solvent, the n.m.r. spectrum of the extract showed that t-butyl acetate was present [singlet (3H) at τ 8·09 and singlet (9H) at τ 8·56]; its yield was determined by integration of the signals and comparison with other components of the mixture. 2,2,3,3-Tetramethylbutane, which was synthesised by Flood and Calingaert's method,[21] was shown not to be present as a reaction product by the absence of the appropriate peak on g.l.c. and the absence of a resonance at τ 9·14 in the n.m.r. spectrum described above.

(d) *t-Butyldiphenylmethanol.* The alcohol (1·20 g.) was treated with lead tetra-acetate (2·28 g.). 1,2-Dibromo-2-methylpropane and t-butyl acetate were estimated as described above, and benzophenone was isolated by preparative g.l.c. (silicone oil, 200°) and was estimated by analytical g.l.c. (silicone oil, 180°) with bibenzyl as standard.

(e) 2-p-*Anisyl*-1,1-*diphenylethanol.* The alcohol (1·52 g.) was treated with lead tetra-acetate (2·28 g.). 4-Methoxybenzyl acetate and benzophenone were isolated by preparative g.l.c. (silicone oil, 200°) and their identities were confirmed by n.m.r. and i.r. spectroscopy as above. 4-Methoxybenzyl chloride (from reaction in carbon tetrachloride) was partially degraded under g.l.c. conditions,[22] although its presence was detected by its retention time on two columns. Its yield was assessed as follows. The reaction product was treated with anhydrous sodium acetate (0·5 g.) in acetic acid (5 ml.) and heated under reflux for 5 hr. It was poured into water, and the ether extract was washed with sodium hydrogen carbonate solution and with water and dried ($MgSO_4$). After evaporation of the solvent, g.l.c. showed that the yield of 4-methoxybenzyl acetate had increased relative to that in an untreated sample, 4-methoxybenzyl chloride was no longer present, and the yield of benzophenone was unchanged; the yield of 4-methoxybenzyl chloride was then estimated by difference. *p*-Anisaldehyde (from reactions in acetic acid) was not isolated, but its presence was indicated both by its retention time on two columns and by the n.m.r. spectrum of the reaction product which showed the low-field aldehydic-proton resonance at τ 0·13 characteristic of this compound. Quantitative g.l.c. was at 180° with biphenyl as standard.

(f) 1-p-*Anisyl*-2-*phenylethanol.* The alcohol (2·26 g.) was treated with lead tetra-acetate (4·66 g.). 4-Methoxydeoxybenzoin (1·16 g.) was isolated from the reaction in benzene–pyridine (1 : 1, v/v) and, after three recrystallisations from methanol, had m.p. 72—72·5° (lit.,[23] 77°) (Found: C, 79·5; H, 6·25. Calc. for $C_{15}H_{14}O_2$: C, 79·6; H, 6·2%) and gave an oxime, m.p. 115° (lit.,[24] 114°). Benzaldehyde, benzyl acetate, and *p*-anisaldehyde were isolated by preparative g.l.c. (silicone oil, 200°) and were identified by their n.m.r. and i.r. spectra, as above. *p*-Anisaldehyde and 4-acetoxyanisole (from reaction in acetonitrile) had identical retention times on all columns tried (silicone oil, Carbowax, Apiezon L, and diethylene glycol polyadipate). The n.m.r. spectrum of the *p*-anisaldehyde fraction (from reaction in acetonitrile) showed that this contained *ca.* 4% of 4-acetoxyanisole, the remainder being *p*-anisaldehyde. Phenylacetaldehyde, *p*-methoxyphenol, diphenylmethane, and bibenzyl were not isolated, but their presence was indicated by g.l.c. retention times on at least two columns. Quantitative g.l.c. was at 180° with benzophenone as standard.

(g) α-*t-Butyl*-4-*methoxybenzyl alcohol.* The alcohol (0·97 g.) was treated with lead tetra-acetate (2·28 g.). *p*-Anisaldehyde and *p*-anisyl t-butyl ketone were isolated by preparative g.l.c. and identified by comparison with the authentic materials, as above. Quantitative g.l.c. was on silicone oil and Carbowax, with biphenyl as standard.

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