Reactions of Lead Tetra-acetate. Part XXI.[1] Acyloxylation, Plumbylation, and Oxidative Dimerisation of Some Benzenoid Compounds in the Presence of Trifluoro- or Trichloro-acetic Acid

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The oxidation of benzene, chlorobenzene, toluene, and anisole by lead tetra-acetate in trifluoroacetic acid or, in some cases, trichloroacetic acid has been studied. The products include biaryls, aryl trifluoroacetates (usually analysed as phenols), aryl acetates, and aryl-lead compounds, in proportions which vary markedly with the aromatic compound and the conditions; for example, in trifluoroacetic acid, benzene gives phenol in up to *ca.* 80% yield whereas anisole gives mainly the dimethoxybiphenyls, and in trichloroacetic acid anisole gives about 50% of bis-*p*-methoxyphenyl-lead bistrichloroacetate, the reactions of which are discussed. Evidence is adduced for the occurrence of two oxidation pathways. One involves electrophilic plumbylation of the aromatic compound, which can be followed by heterolysis to give an aryl cation; the other is a process involving, formally, electron-transfer from the aromatic compound to lead(IV). The relative importance of the two not only depends on the electron-releasing ability of the benzenoid substituents but is also sensitive to the acid strength of the medium.

We have shown previously that benzenoid compounds which are particularly reactive towards electrophilic reagents can react with lead tetra-acetate in two ways, namely, by plumbylation, which corresponds to substitution at lead(IV) and is readily reversible, and by acetoxylation, which is accompanied by reduction of lead(IV) to lead(II).[2,3] The substituents on the aromatic ring have a marked influence in determining which of the two reactions dominates; for example, *m*-dimethoxybenzene, which is more reactive than its *ortho*- or *para*-isomers in those substitutions which occur by the S_E2 mechanism, undergoes plumbylation more readily than its isomers, whereas the latter undergo acetoxylation the more readily.[3] Benzene is barely affected by lead tetra-acetate under the conditions used in these experiments, but Partch has shown that benzene is oxidised readily at room temperature by lead tetrakistrifluoroacetate[4] and we have found that a solution of lead tetra-acetate in trifluoroacetic acid oxidises tetramethylsilane.[5] This notable increase in the oxidising power of lead(IV) in the presence of trifluoroacetic acid prompted us to study the behaviour of benzene and some monosubstituted derivatives towards lead tetra-acetate in trifluoroacetic acid in the hope of learning more about the factors which control the relative ease of plumbylation and acyloxylation; we were led also to the use of trichloroacetic acid in place of the trifluoro-compound. In each case small amounts of chlorinated derivatives were formed, presumably owing their origin to the chloride-ion impurity in commercial lead tetra-acetate even after recrystallisation,[3] but mention of these is omitted from the discussion for simplicity. The lead tetra-acetate was slightly moist with acetic acid after purification, but (except where stated) no attempt was made to dry it thoroughly because of the rapid hydrolysis in air which then ensues. Yields are based on lead tetra-acetate unless stated otherwise.

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[1] Part XX, M. J. Harrison and R. O. C. Norman, *J. Chem. Soc.* (*C*), 1970, 728.

[2] D. R. Harvey and R. O. C. Norman, *J. Chem. Soc.*, 1964, 4860.

[3] R. O. C. Norman and C. B. Thomas, *J. Chem. Soc.* (*B*), 1970, 421.

[4] R. E. Partch, *J. Amer. Chem. Soc.*, 1967, **89**, 3662.

[5] R. O. C. Norman and M. Poustie, *J. Chem. Soc.* (*C*), 1969, 196.

Reactions of Benzene and Some Monosubstituted Derivatives.—(a) *Benzene.* Benzene was oxidised by lead tetra-acetate in trifluoroacetic acid at room temperature to give phenyl trifluoroacetate, phenyl acetate, acetic acid, and, under some conditions, biphenyl. Work-up with M-sodium hydroxide removed the acid and effected hydrolysis of phenyl trifluoroacetate, but not phenyl acetate, to phenol. The results are in Table 1.

TABLE 1

Products from the oxidation of benzene with lead tetra-acetate in trifluoroacetic acid

Mol ratio of reactants		Products (mol %)		
$PhH : Pb^{IV}$	$CF_3{\cdot}CO_2H : Pb^{IV}$	PhOH	PhOAc	PhPh
1·1	11	46	5	
1·0	40	54	0·8	
37	22	62	1·5	3·8
62	26	48	1·4	7·0

TABLE 2

Oxidation of benzene (0·112 mol) with lead tetra-acetate ($5{\cdot}2 \times 10^{-5}$ mol) in trifluoroacetic acid (0·129 mol) with added acetic acid

Mol ratio *	Products (mol %)			Mol ratio
$HOAc : CF_3{\cdot}CO_2H$	PhOH	PhPh	PhOAc	PhOAc : PhOH
0·019	62	6·4	0·1	0·002
0·044	54	4·9	0·2	0·004
0·070	49	3·8	0·3	0·006
0·096	48	3·5	0·4	0·008
0·122	48	3·6	0·6	0·013
0·148	47	3·9	1·0	0·021
0·216	46	5·1	2·1	0·046
0·256	48	5·3	2·2	0·046
0·299	44	5·4	3·4	0·077

* This includes the acetic acid available from the lead(IV) ligands.

These data suggest that, first, there are competitive reactions between trifluoroacetate and acetate groups leading ultimately to phenol and phenyl acetate, respectively, and secondly, that biphenyl may be removed by further oxidation unless there is a large excess of benzene to consume the oxidant. We carried out two systematic series of experiments to examine these aspects further (Tables 2 and 3); a sample of lead tetra-acetate which had been freed of acetic acid was used so that the ratio of the total available amounts of acetate and trifluoroacetate groups was known.

The results in Table 2 show that the total yield of products falls as the amount of acetic acid present is increased. At the same time, the yield of phenyl acetate rises relative to that of phenol; however, while the ratio of the two is approximately proportional to that of the available amounts of acetate and trifluoroacetate groups, it is notable that the former ratio is much smaller than the latter (see later).

As the concentration of benzene is increased, the yield of biphenyl increases (Table 3). However, except when large amounts of benzene are included, the proportional increase in the ratio of the yield of biphenyl to that of phenol and phenyl acetate is larger than that in the concentration of benzene; that is, the yield of biphenyl at low concentrations of benzene is relatively small even when allowance is made for the fact that formation of biphenyl requires two molecular equivalents of benzene and that of phenol or phenyl acetate requires only one. It is therefore probable that biphenyl is relatively easily removed by further oxidation (as would be expected from the selectivity of the oxidant, described later, and the fact that biphenyl is more reactive than benzene towards electrophiles); this removal will become relatively less important as the amount of benzene is increased compared with that of oxidant and thence available biphenyl.

When trifluoroacetic acid was replaced by trichloroacetic acid, with a 30-fold mol excess of benzene over lead tetra-acetate, there was no reaction at room temperature, but at 75° the solution darkened within a few hours and a small quantity of lead(II) salts was deposited. Biphenyl (0·9%), phenyl trichloroacetate, and phenyl acetate were formed, and after hydrolysis of the esters 27% of phenol was obtained.

TABLE 3

Oxidation of benzene with lead tetra-acetate (8×10^{-4} mol) in trifluoroacetic acid (0·131 mol)

PhH added (ml)	Mol ratios		Products (mol %)			Mol ratios	
	$PhH : CF_3{\cdot}CO_2H$	$PhH : Pb^{IV}$	PhOH	PhOAc	PhPh	PhPh : PhOH	PhOAc : PhOH
1	0·086	13·8	65	0·28	$<0{\cdot}03$	$<0{\cdot}0005$	0·004
2	0·172	27·6	64	0·21	0·18	0·003	0·003
5	0·430	69	63	0·19	3·2	0·05	0·003
10	0·86	138	61·5	0·18	6·8	0·11	0·003
25	2·15	345	57	0·17	13·9	0·24	0·003
50	4·3	690	52	0·12	18·5	0·35	0·002
100	8·6	1380	26	$<0{\cdot}1$	22·5	0·87	

(b) *Chlorobenzene.* Chlorobenzene reacted relatively slowly with lead tetra-acetate in trifluoroacetic acid, even at 80°. After 4 h at this temperature, hydrolysis yielded 11% of *p*-chlorophenol and traces of phenol and *o*-chlorophenol. Comparison with the conditions used for the oxidation of benzene indicates that the reagent is relatively selective, and we attempted to determine the selectivity[6] quantitatively by oxidising an equimolar mixture of benzene and chlorobenzene with less than the required amount of lead tetra-acetate and determining the amounts of unchanged aromatic

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[6] L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, **1**, 35.

compound.[7] However, the method proved inaccurate because so small a proportion of the chlorobenzene was consumed compared with benzene; it was possible to conclude only that benzene was consumed at least twenty times as rapidly as chlorobenzene.

(c) *Toluene.* The addition of toluene to a solution of lead tetra-acetate in trifluoroacetic acid caused an exothermic reaction which gave, after hydrolytic work-up, the cresols, three of the bitolyls, and phenyl-*p*-tolylmethane (Table 4, experiment 1); benzyl acetate, trifluoroacetate, or alcohol were not present in greater than 0·2% yield as estimated by g.l.c., and bi-*o*-tolyl was not detected. The evolution of heat in this reaction was reduced by the dropwise addition of a solution of lead tetra-acetate in trifluoroacetic acid to an excess of toluene at 0°; the yield of bitolyls was increased considerably (Table 4, experiments 2—4), but side-chain oxidation products were again negligible.

Toluene did not react at a significant rate with lead tetra-acetate in the presence of trichloroacetic acid at room temperature, but after 9 days at 50° extensive oxidation had occurred; the products, after hydrolytic work-up, were the cresols (*o*-, 1·8; *m*-, 1·6; *p*-, 31%), three of the bitolyls (2,4'-, 10; 3,4'- and 4,4'-, 10% in all), and a mixture of the cresyl acetates (3%). 2-Hydroxy-5-methylbenzaldehyde (9%) and 4-dichloromethyl-4-methylcyclohexa-2,5-dienone (6%) were also obtained, probably as the result of Reimer–Tiemann reactions during work-up, for each was also formed when a mixture of *p*-cresol and trichloroacetic acid was submitted to the hydrolytic work-up procedure.

TABLE 4

Products from the oxidation of toluene with lead tetra-acetate in trifluoroacetic acid

	Mol ratios of reactants		Products (mol %)				
					Bitolyls		
Expt.	PhMe : $Pb(OAc)_4$	$CF_3\cdot CO_2H$: $Pb(OAc)_4$	*m*- + *p*-Cresol	*o*-Cresol	2,4'	3,4' + 4,4'	*p*-TolylCH_2Ph
1	5	24	24	4·3	3	1·5	0·6
2	24	20	21	3·8	15	10	0·6
3	39	23	23	4·4	19	13	0·7
4	39	41	21 *	6·4	15	8·2	0·2

* Further analysis showed that the ratio of *m*- to *p*-cresol was 1 : 25.

(d) *Anisole.* Reaction with lead tetra-acetate in trifluoroacetic acid at room temperature was vigorous; the solution turned black and the temperature rose to *ca.* 60°. Heat was also evolved when anisole was added dropwise to the solution of the oxidant at 0°; after treatment with aqueous sodium hydrogen carbonate, *p*-methoxyphenol (0·3%), 4,4'-dimethoxybiphenyl (0·9%), 2,4'-dimethoxybiphenyl (0·6%), and a trace of 2,2'-dimethoxybiphenyl were obtained. However, suitable control of the reaction was effected by the dropwise addition of the oxidant solution to excess of anisole at 0°; the temperature did not rise appreciably and the solution remained deep green for several hours. The total yield of the dimethoxybiphenyls was thereby raised to *ca.* 35% (4,4'-, 20·5; 2,4'-, 13; 2,2'-, 0·5%), but the yield of *p*-methoxyphenol increased less, to 0·7%, and there was only a trace of *o*-methoxyphenol. Neither bis(methoxyphenyl)methanes nor 3,4'-dimethoxybiphenyl were detectable. When benzene was also included, in equimolar amount to anisole, the yields of these products were essentially unchanged and a very small amount of 4-methoxybiphenyl (*ca.* 0·05%) (but no 2-methoxybiphenyl) was also detected. The green colour characteristic of these reactions was also obtained when a mixture of 2,4'- and 4,4'-dimethoxybiphenyl was oxidised with lead tetra-acetate in trifluoroacetic acid and it was shown, by e.s.r.[8] and electronic spectroscopy, that the radical-cation of the latter was present.

The addition of excess of anisole to a mixture of lead tetra-acetate and trichloroacetic acid at room temperature gave a blue-green colour and the solution turned black after a few minutes. After the solution had been stirred for some hours, a flocculent white precipitate formed; it was filtered off after about 72 h, when precipitation appeared to be complete. The material, which discoloured above 200° and decomposed at *ca.* 265°, gave analytical data consistent with it being a bis-methoxyphenyl-lead bistrichloroacetate, and integration of its ^{1}H n.m.r. spectrum, measured in the presence of a standard, showed that it contained 0·9% of methyl-protons as compared with 0·8% required for this structure; on the basis of this structure, its yield was 48%. The compound was insoluble in water or anisole, and only sparingly soluble in ether, benzene, or chloroform. It dissolved in ethanol, presumably as the result of ligand-exchange, but its solution in pyridine, dimethylformamide, or dimethyl sulphoxide set to a gel within 5 min (*cf.* the behaviour of phenyllead triacetate [9]).

In order to determine the orientation of the methoxyphenyl groups in the lead compound, the material was treated with iodine in benzene for 12 h. Iododeplumbylation occurred (*cf.* iododestannylation of compounds of the type [10] $ArSnR_3$), and *p*-iodoanisole was obtained in 99 ± 3% yield (based on two methoxy-

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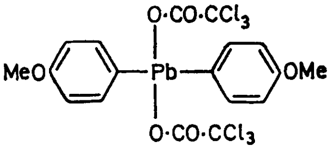
[7] C. K. Ingold, A. Lapworth, E. Rothstein, and D. Ward, *J. Chem. Soc.*, 1931, 1959.

[8] W. F. Forbes and P. D. Sullivan, *Canad. J. Chem.*, 1968, **46**, 325.

[9] H. Shapiro and F. W. Frey, 'The Organic Compounds of Lead,' Interscience, New York, 1968, p. 298.

[10] R. O. C. Norman and R. Taylor, 'Electrophilic Substitution in Benzenoid Compounds,' Elsevier, 1965, p. 273.

phenyl residues per molecule of the lead compound). *o*-Iodoanisole, of which less than 0·5% would have been detected, was not found, so that we infer that the lead compound is bis-*p*-methoxyphenyl-lead bistrichloroacetate (I).



(I)

The solution from the lead(IV) oxidation, after removal of compound (I) and hydrolysis, was found to contain small amounts of four dimethoxybiphenyls (2,4′-, 3·2; 4,4′-, 1·3; 2,2′-, 0·22; 3,4′-, 0·1%), bis-(*p*-methoxyphenyl)methane (0·35%), a trace of *o*-methoxyphenyl-(*p*-methoxyphenyl)methane, and *o*- (0·1%) and *p*-methoxyphenol (0·2%). In another experiment, in which the lead derivative (I) was not filtered off, it was found that the precipitate slowly dissolved during 6 weeks to give, after hydrolysis, the same products as before.

When oxidation was conducted with excess of an equimolar mixture of anisole and benzene in the presence of trichloroacetic acid at room temperature, the yields of the lead derivative (I) which precipitated and of the methoxyphenyl derivatives in the filtrate were in approximately the same ratios as those just quoted but, in addition, as much 4-methoxybiphenyl as 4,4′-dimethoxybiphenyl was formed.

The lead derivative (I) decomposed at room temperature in trifluoroacetic acid to give anisole (26%), *p*-methoxyphenol (1·7%), 2,2′-, 2,4′-, and 4,4′-dimethoxybiphenyl (Table 5), traces of 3,4′-dimethoxybiphenyl and *o*-methoxyphenyl-(*p*-methoxyphenyl)- and bis-(*p*-methoxyphenyl)-methane, and some unidentified, less volatile materials. The inclusion of anisole in the trifluoroacetic acid led to both an increase in the total yield of dimethoxybiphenyls and a change in the ratio of 4,4′- to 2,4′-dimethoxybiphenyl (Table 5); in addition to the three dimethoxybiphenyls tabulated, 3,4′-dimethoxybiphenyl was formed in amounts which increased (from *ca.* 0·1 to 2%) with successive increase in the concentration of anisole, although not so markedly as the yield of the 4,4′-isomer. As the ratio of [PhOMe] to [(I)] was increased, the reaction became slower and the proportion of coloured, non-volatile products was reduced.

TABLE 5

Variation of the yields of 2,2′-, 2,4′- and 4,4′-dimethoxybiphenyl from decomposition of the compound (I) with added anisole

Mol ratio [PhOMe] : [(I)]	Yield (mol %) of dimethoxybiphenyls 2,2′-	2,4′-	4,4′-	Ratio of yields of 4,4′- to 2,4′-dimethoxybiphenyl
0	0·08	0·7	0·09	0·13
15	0·2	4·0	0·9	0·225
35	0·3	7·3	2·0	0·27
58	0·4	8·3	2·9	0·35
142	0·6	11·6	5·5	0·48
317	1·0	14·7	11·5	0·78
540	1·9	21·4	18·6	0·87
1360	3·2	22·7	20·6	0·91

Mechanisms of Oxidation.—(i) *Anisole*. The formation of the lead derivative (I) by oxidation in trichloroacetic acid is consistent with the occurrence of successive electrophilic plumbylations.[2,3] Reaction of this type is usually readily reversible in the presence of acid, and we infer that the production of anisole from the compound (I) with trifluoroacetic acid occurs, at least in part,[3] by protodeplumbylation, reaction (1).

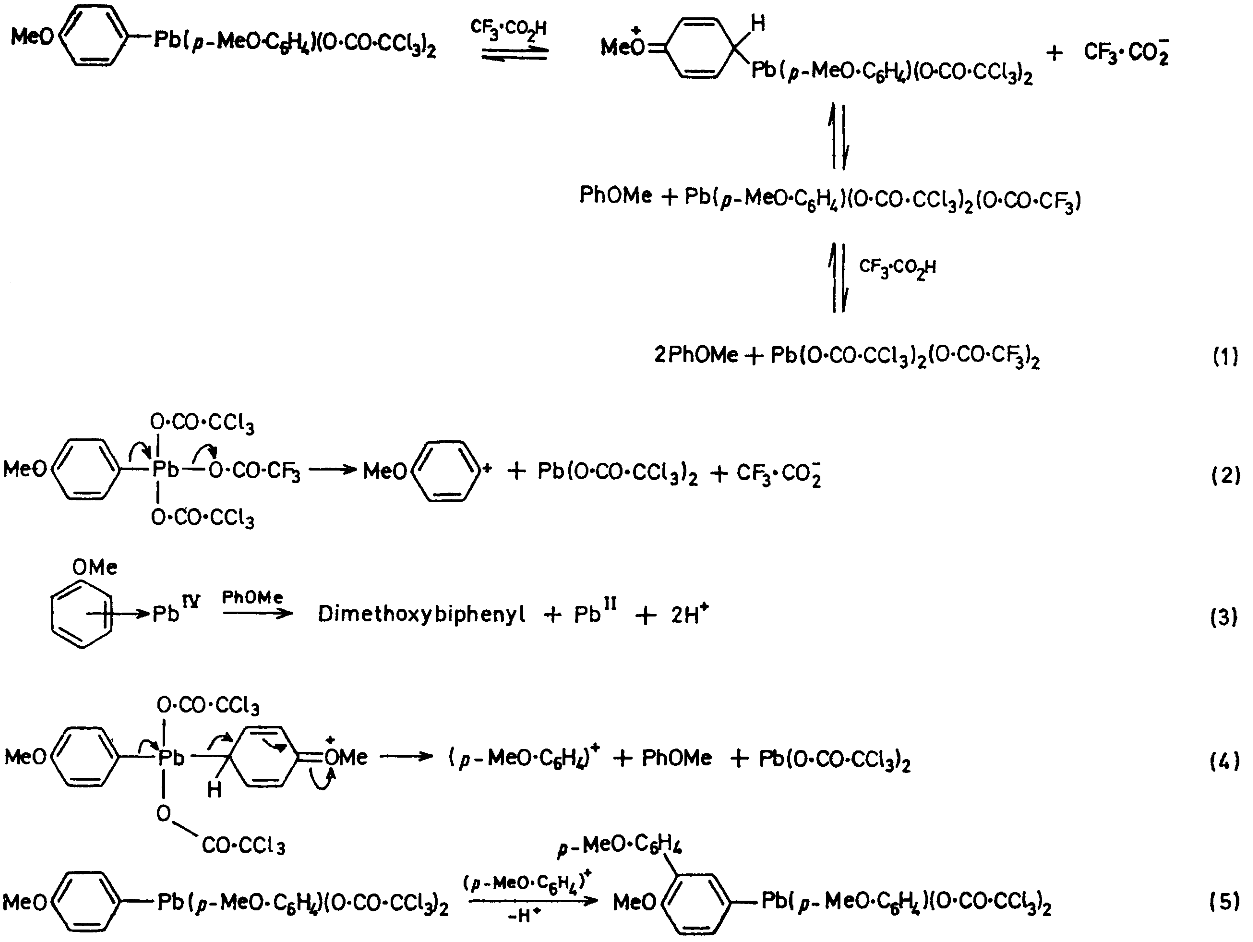
We believe, for the reasons discussed later, that compound (I) mediates in the formation of the dimethoxybiphenyls in two ways, depending upon the conditions. First, it acts as a source of *p*-methoxyphenyl cations [*e.g.*, reaction (2)] which can effect substitution either in anisole or in the lead derivative (I) (see later). Secondly, it provides a source of lead(IV) for the oxidation of anisole by the electron-transfer mechanism previously suggested to account for the acetoxylation of the dimethoxybenzenes;[3] in this case, nucleophilic attack by one molecule of anisole on a second molecule from which electrons are removed by lead(IV) leads to the dimers [*e.g.*, reaction (3) and see later]. There is also the possibility that protonation of the lead compound (I) leads to the simultaneous production of anisole and a *p*-methoxyphenyl cation, reaction (4).

TABLE 6

Variation of the yields of dimethoxybiphenyls and 4-methoxybiphenyl from decomposition of the compound (I) with addition of equimolar amounts of anisole and benzene

Mol ratio [PhOMe] = [PhH] : [(I)]	Yields (mol %) Dimethoxy-biphenyls (a) 2,2′	2,4′	4,4′	4-MeO·C_6H_4·Ph (b)	Ratio (a) : (b)
8·2	0·2	2·6	0·3	0·75	4·1
25	0·4	6	1·5	0·9	8·8
177	1·0	14	8·5	1·0	23·5

That there are at least two pathways leading from the lead compound (I) to the dimers is shown by the variation in the ratio of the amounts of 2,4′-, 3,4′-, and 4,4′-dimethoxybiphenyl formed when this compound is treated with trifluoroacetic acid containing different amounts of added anisole (Table 5). To investigate this further, we decomposed the compound (I) in trifluoroacetic acid containing various amounts of an equimolar mixture of benzene and anisole. As the data in Table 6 show, the ratio of dimethoxybiphenyls to 4-methoxybiphenyl increases markedly as increasing amounts of benzene and anisole are added; thus, a reagent is responsible for the arylation of anisole or benzene when large amounts of these materials are included which is more selective than that involved when only small amounts are present.



Scheme 1

Analogy with the formation of the phenyl cation from phenyl-lead triacetate with boron trifluoride[11] indicates that one possible arylating agent derived from the compound (I) with trifluoroacetic acid is the *p*-methoxyphenyl cation. We suggest that this is the principal arylating entity when no anisole is added to the mixture, for the following reasons. First, the *p*-methoxyphenyl cation would be expected to resemble the phenyl cation in being extremely reactive and comparatively unselective between different nucleophiles.[11,12] Anisole is only about 50% more reactive than benzene towards the latter cation,[11,12] and the selectivity of the arylating agent is greater than this under our conditions, even for the smallest amount of added benzene and anisole in Table 6; it is far greater when large quantities of benzene and anisole are added. Secondly, there is no reason why formation and reaction of the *p*-methoxyphenyl cation should become increasingly important when anisole, or anisole and benzene, are added to the trifluoroacetic acid; indeed, the opposite would be expected because the solvent becomes less polar. However, we should expect the alternative pathway to become more significant with increase in the amount of added anisole since we believe this to be a reaction of higher order with respect to anisole (see later).

The *p*-methoxyphenyl cation would be expected to react not only with the anisole formed by protodeplumbylation [reaction (1)] and with added anisole, to give 2,4'-, 3,4'-, and 4,4'-dimethoxybiphenyl, but also with the compound (I), as in reaction (5), to give the first two of these three dimethoxybiphenyls after protodeplumbylation. This may underlie the steady increase in the ratio of 4,4'- to 2,4'-dimethoxybiphenyl with increase in the amount of added anisole (Table 5), since the latter pathway, which cannot give 4,4'-dimethoxybiphenyl, would become less important. Neither pathway can account for the formation of 2,2'-dimethoxybiphenyl, but the labelling experiments described later indicate possible mechanisms for the formation of this isomer.

Methoxyphenyl cations should be effective reagents for removing hydride ion from suitable donors, and such a reaction may underlie the formation of *o*-methoxyphenyl-(*p*-methoxyphenyl)- and bis-(*p*-methoxyphenyl)-methane. Thus, the phenoxymethyl cation should be energetically preferred to a methoxyphenyl cation, allowing the hydride-transfer in Scheme 2, and this cation, pos-

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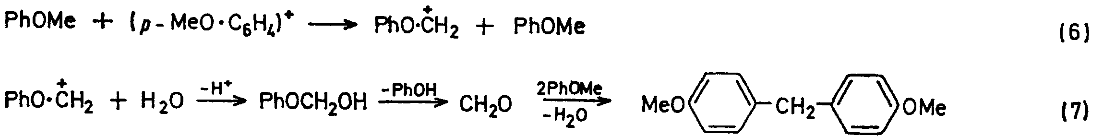
[11] J. B. Aylward, *J. Chem. Soc.* (*B*), 1967, 1268.

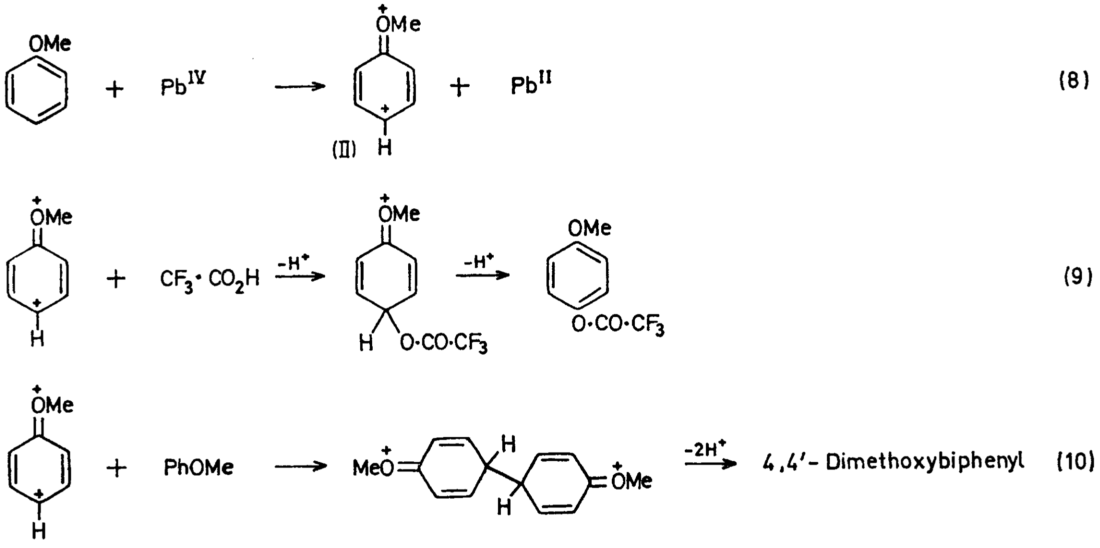
[12] R. A. Abramovitch and J. G. Saha, *Canad. J. Chem.*, 1965, **43**, 3269.

sibly by reaction with adventitious water present in the very hygroscopic trifluoro- and trichloro-acetic acids, could give formaldehyde and thence, by reaction with anisole, the bis(methoxyphenyl)methanes (Scheme 2). [Reaction of formaldehyde with phenol might also be expected, but anisole was always likely to be in excess and in any case phenol should be oxidised very rapidly by the lead(IV) species.] Consistent with this view, when a mixture of anisole and formaldehyde was stirred in the presence of trifluoroacetic acid for 12 h, the major products were bis-(*p*-methoxyphenyl)methane and the *o,p'*-isomer, in the ratio 8 : 1.



SCHEME 2

It has previously been suggested that the acetoxylation of anisole and the dimethoxybenzenes by lead tetra-acetate in acetic acid occurs by nucleophilic attack by the solvent on an aromatic ring from which, formally, one or two electrons have been removed by the oxidant.[3] The ability of lead(IV) to accept electrons in this way should be enhanced by increase in the electronegativity of the lead(IV) ligands or by acid-catalysis of the removal of a ligand with its bonding-pair; in either case, reaction should occur more readily in the presence of trifluoroacetic acid compared with trichloroacetic or acetic acid since it is the strongest acid of the three and provides the most electronegative ligand. We therefore envisage the formation of *p*-methoxyphenyl trifluoroacetate and the dimethoxybiphenyls from the compound (I), following protodeplumbylation with trifluoroacetic acid, as occurring by reaction (8) followed by (9) or (10) (with related reactions accounting for 2,2'- and 2,4'-dimethoxybiphenyl), although it must be emphasised, first, that we cannot distinguish between a two-electron oxidation as shown or successive one-electron oxidations[3] and, secondly, that the species (II) is not necessarily a free entity; that is, removal of electrons from the aromatic ring may be synchronous with nucleophilic attack.



The reaction of anisole with lead tetra-acetate in trifluoroacetic acid yields, after work-up, 2,2'-, 2,4'-, and 4,4'-dimethoxybiphenyl, and *p*-methoxyphenol. We infer that these are formed by the electron-transfer process, and not *via* methoxyphenyl cations, for the following reasons. First, no bis(methoxyphenyl)methanes were detected, whereas these are formed under the conditions in which we believe the *p*-methoxyphenyl cation mediates. Secondly, the absence of 3,4'-dimethoxybiphenyl, and the very large ratio of the amounts of the dimethoxybiphenyls and 4-methoxybiphenyl formed when an equimolar mixture of anisole and benzene was included (*ca.* 700 : 1), indicate that the arylating reagent has a very much greater selectivity than we attribute to methoxyphenyl cations.

Reaction of anisole with lead(IV) in trichloroacetic acid gives a significant yield of the lead(IV) derivative (I) and only traces of dimethoxybiphenyls, suggesting that electrophilic plumbylation occurs in preference to the electron-transfer process, in contrast to the course of the reaction in trifluoroacetic acid. In order to determine whether this difference results from specific properties of the acids used or from their different acid strengths, we studied the oxidation of an equimolar mixture of anisole and benzene in trifluoroacetic acid containing various amounts of acetic acid. The results in Table 7 show that, as the ratio of total available acetic acid to trifluoroacetic acid is increased from about 0·3 : 1 to 1·6 : 1, the ratio of the yield of dimethoxybiphenyls to that of 4-methoxybiphenyl decreases steadily from *ca.* 650 : 1 to 1·7 : 1 and 3,4′-dimethoxybiphenyl and the two bis(methoxyphenyl)methanes are only formed in the presence of relatively large amounts of acetic acid. These trends indicate that oxidation occurs mainly by the electron-transfer mechanism when little acetic acid is present and mainly *via* the methoxyphenyl cation when more acetic acid is added. Since reaction is much faster under all these conditions than when acetic acid alone is the solvent,[2] we infer that the generation of methoxyphenyl cations by electrophilic plumbylation followed by heterolysis of the aryl–Pb bond, as well as the electron-transfer process, is catalysed by trifluoroacetic acid but that the latter reaction is the more sensitive of the two to such catalysis.

TABLE 7

Products (mol %) from the oxidation of anisole and benzene in trifluoroacetic acid with added acetic acid [a]

Mol ratio [b] HOAc : $CF_3{\cdot}CO_2H$	Dimethoxybiphenyls 2,2′-	2,4′-	4,4′-	3,4′- [c]	$4\text{-MeO}{\cdot}C_6H_4{\cdot}Ph$	$(4\text{-MeO}{\cdot}C_6H_4)_2CH_2$	Ratio [d]
0·319	0·37	13·4	18·9		0·05		650
0·363	0·42	11·8	12·9		0·30		84
0·401	0·45	10·9	9·5	Trace	1·1	Trace	19
0·590	0·21	4·5	0·75	0·44	2·1	0·49	2·6
1·61	0·12	3·25	0·46	0·50	2·2	0·60	1·7

[a] No biphenyl was detected in any experiment; the yields of *p*-methoxyphenol and *p*-methoxyphenyl acetate were always less than 0·5 and 0·2%, respectively. [b] See footnote to Table 2. [c] Together with *o*-methoxyphenyl-(*p*-methoxyphenyl)methane. [d] Ratio of yield of 2,2′-, 2,4′-, and 4,4′-dimethoxybiphenyl to 4-methoxybiphenyl.

Some other aspects of the formation of dimethoxybiphenyls were examined by carrying out the decomposition of the lead derivative (I) in trifluoroacetic acid containing *m*-deuterioanisole (the sample of which contained 12% of unlabelled material); the mol ratio of *m*-deuterioanisole to (I) was 385 : 1. The proportions of each of 2,2′-, 2,4′-, and 4,4′-dimethoxybiphenyl containing none, one, or two deuterium atoms were measured by mass spectrometry (Table 8).

TABLE 8

Percentage of deuterated dimethoxybiphenyls from the acid-catalysed decomposition of the lead-derivative (I) in the presence of *m*-deuterioanisole

Dimethoxybiphenyl	Rel. yield of the dimethoxybiphenyl	Percentage of molecules containing 0, 1, or 2 deuterium atoms		
		0	1	2
2,2′	0·07	5	29	66
2,4′	1	9	61	30
4,4′	0·8	8	68	24

The following inferences can be drawn. (a) Exchange reactions between the lead derivative (I) and anisole, such as reaction (11), cannot be as rapid as the rate at which dimethoxybiphenyls are formed since, if they were, the proportion of each dimethoxybiphenyl containing none, one, and two deuterium atoms would be 1·4, 21·1, and 75·5%, respectively.* (b) The very low proportion of each dimethoxybiphenyl which contains no deuterium atoms shows that intramolecular rearrangement of the compound (I) to give a dimethoxybiphenyl and lead(II) cannot be a significant pathway (at least under the conditions used), although its occurrence cannot be ruled out. (c) The large fraction of 2,2′-dimethoxybiphenyl containing two deuterium atoms shows that much of this compound is derived from two molecules of the solvent. This could involve replacement of a *p*-methoxyphenyl residue in the lead derivative (I) by a deuteriated *o*-methoxyphenyl group followed by generation of an *o*-methoxyphenyl cation and its reaction with deuteriated anisole [*cf.* reaction (11)], but in view of the conclusion in (a) it is likely that other pathways are also important; one such is the electron-transfer process, and a second is reaction of a *p*-methoxyphenyl cation derived from the compound (I) with deuteriated anisole to give a deuteriated *o*-methoxyphenyl cation, reaction (12), followed by electrophilic substitution in another deuteriated anisole. (d) The predominance of monodeuteriated 2,4′- and 4,4′-dimethoxybiphenyl over the dideuteriated analogues suggests that reaction of a *p*-methoxyphenyl cation from the compound (I) with deuteriated anisole is more important than the electron-transfer process under these conditions. Since the *o*-methoxyphenyl cation, which we believe mostly to be deuteriated, can form 2,4′-dimethoxybiphenyl as well as the 2,2′-isomer by reaction with the solvent, it is reasonable that the ratio of mono- to di-deuteriated dimethoxybiphenyl is smaller for the 2,4′- than for the 4,4′-isomer.

(ii) *Benzene.* It was noted earlier that benzene is consumed at least twenty times as rapidly as chlorobenzene by lead tetra-acetate in trifluoroacetic acid. Since the oxidation of mixtures of anisole and (the less reactive) benzene in the presence of various amounts of acetic acid gave helpful information about the modes of oxidation of anisole, we carried out similar competitive experiments with mixtures of benzene and chlorobenzene

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* This follows from the deuterium content of the added anisole, the statistical distribution being as $12^2 : 2 \times 12 \times 88 : 88^2$. [The amount of unlabelled anisole available from the compound (I) is only 0·5% of the total anisole.]

in the hope of gaining information about the mechanism of oxidation of benzene. The results are in Table 9; under the conditions of these experiments neither chlorophenols nor dichlorobiphenyls were formed in other than negligible amounts.

It is apparent from these data that the much greater rate of consumption of benzene than chlorobenzene is associated mainly with the considerably greater rate of formation of phenyl trifluoroacetate (isolated as phenol) than its chloro-substituted derivatives. In contrast, the selectivity shown in the formation of biphenyl compared with the chlorobiphenyls is relatively small. These observations are accommodated by the view that a reactive entity is generated from benzene far more readily than from chlorobenzene; this species then reacts preferentially with trifluoroacetate groups, but can also react with benzene or chlorobenzene to give the biaryls (and shows a fairly small selectivity in this respect) or with acetate groups. Analogy with the behaviour of anisole suggests that the reactive entity is either the phenyl cation, formed by way of a phenyllead tetracarboxylate, or a benzene ring from which, formally, one or two electrons have been removed by the oxidant; in each case, benzene would be expected to be more reactive than chlorobenzene. Further analogy suggests that each of these entities plays a part; thus, the addition of acetic acid is accompanied in each case by a decrease in the selectivity of the arylation process, from which we infer that, for the reaction of benzene, arylation *via* the phenyl cation becomes increasingly important relative to that *via* an electron-deficient benzene species as the concentration of acetic acid is increased.

Table 9

Products from the oxidation of benzene and chlorobenzene (0·105 mol of each) with lead tetra-acetate ($5{\cdot}2 \times 10^{-5}$ mol) in trifluoroacetic acid (0·129 mol) with added acetic acid

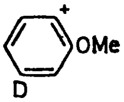
Mol ratio [a] HOAc : $CF_3\cdot CO_2H$	Products (mol %) PhOH	PhOAc	PhPh	o-ClC_6H_4-Ph	ClC_6H_4-Ph [b]
0·019	85		4·6	0·8	0·5
0·032	81		3·9	0·8	0·5
0·057	73		2·8	0·8	0·4
0·083	58	0·7	2·0	0·9	0·4
0·109	53	1·2	2·2	0·9	0·4
0·148	43	1·3	2·3	0·9	0·4
0·278	51	2·9	2·5	0·9	0·4
0·407	49	4·6	2·1	0·9	0·4

[a] See footnote to Table 2. [b] Total *m*- and *p*-isomers.

Since acetic acid is a stronger nucleophilic reagent than its trifluoro-analogue, it is surprising that the ratio of the yields of phenol and phenyl acetate is greater than that of the available trifluoroacetic acid and acetic acid (Table 9; *cf.* Table 2). The explanation may be that the former acid is extensively ionised under the reaction conditions, the trifluoroacetate anion being a better nucleophile than acetic acid. Moreover, in the case of reactions occurring by the electron-transfer mechanism, it is possible that the removal of electrons from the aromatic ring is synchronous with nucleophilic attack (see earlier); if so, then since the oxidising power of lead(IV) should increase with increase in the number of trifluoroacetate ligands, those lead(IV) molecules which effect oxidation are likely to be associated with a higher ratio of trifluoroacetate to acetate ligands than the ratio of the corresponding acids in solution.

$$(p\text{-MeO}\cdot C_6H_4)_2PbX_2 + m\text{-D}\cdot C_6H_4\cdot OMe \rightleftharpoons (p\text{-}[m\text{-D}\cdot C_6H_3\cdot OMe])(p\text{-MeO}\cdot C_6H_4)PbX_2 + PhOMe \qquad (11)$$

$$(p\text{-MeO}\cdot C_6H_4)^{+} + m\text{-D}\cdot C_6H_4\cdot OMe \rightleftharpoons PhOMe +$$



(12)

The predominance of phenyl trifluoroacetate (and thence phenol) from benzene is in contrast to the preferential formation of the dimethoxybiphenyls from anisole (Table 7). One reason for this is doubtless that the *ortho*- and *para*-carbon atoms in anisole are stronger nucleophiles than the nuclear carbon atoms in benzene and so compete more successfully with trifluoroacetic acid or its anion. However, there are likely to be additional factors since the reaction conditions were not the same for the experiments recorded in Tables 7 and 9. In particular, because of the very high reactivity of anisole, it was necessary to add the solution of oxidant in trifluoroacetic acid dropwise to the aromatic compounds; early in the reaction there would be little trifluoroacetic acid to compete with the anisole as a nucleophile, unlike the conditions for the experiments in Table 9. This may also be responsible in part for the fact that the ratio of the yields of phenol and biphenyl (Table 9) is much greater than unity whereas that of *p*-methoxyphenol to 4-methoxybiphenyl (Table 7) is significantly less. However, another factor in this instance is that the reactivity of 4-methoxybiphenyl compared with anisole should be considerably less than that of biphenyl compared with benzene; thus, further oxidation would reduce the yield of biphenyl proportionately more than that of 4-methoxybiphenyl. Finally, the reduction in the ratio of the yields of biphenyl and the chlorobiphenyls on addition of acetic acid is far smaller than that of the yields of the dimethoxybiphenyls to 4-methoxybiphenyl. It seems probable that, even in the absence of added acetic acid, the oxidation of benzene occurs largely by way of the phenyl cation. Moreover, this is in accord with expectation based on data now available about the role of electron-donating substituents in determining the ease of oxidation of benzenoid compounds by the electron-transfer mechanism. Thus, *o*- and *p*-dimethoxybenzene are readily oxidised in this way at 80° in the absence of trifluoroacetic acid;[3] anisole is somewhat less reactive under these conditions,[3] while at room temperature it apparently reacts in this way only when trifluoroacetic acid is present; benzene would be expected to be still less reactive in the presence of similar concentrations of trifluoroacetic acid.

(iii) *Toluene*. It is reasonable to suppose that toluene, the ability of which to release electrons is intermediate between those of benzene and anisole, likewise undergoes oxidation in the presence of trifluoroacetic acid *via* both tolyl cations and the electron-transfer mechanism. The very much higher ratio of bitolyls to cresols (Table 4) than that of biphenyl to phenol from benzene is consistent with the greater nucleophilicity of the nuclear carbon atoms in toluene compared with those in benzene.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded for solutions in deuteriochloroform (except where stated) on a Perkin-Elmer R10 60 MHz spectrometer. Mass spectra were determined on an A.E.I. MS12 spectrometer which was coupled *via* a heated capillary to a gas chromatograph. E.s.r. spectra were determined on a Varian V4502 spectrometer with 100 kHz modulation and an *X*-band klystron. I.r. spectra were recorded on a Unicam SP 200 spectrophotometer and visible and u.v. spectra were recorded on a Unicam SP 800 spectrophotometer.

Analytical gas chromatography was carried out on a Pye instrument (Series 104, model 24) with 6 ft × $\frac{1}{4}$ in columns usually packed with 10% silicone oil (MS 550) or 10% diethylene glycol adipate (with 2% phosphoric acid), coated on Celite. Quantitative analysis was carried out with the addition of a suitable internal standard; a hydrogen-inject flame ionisation detector gave a linear response, and the relationship between the quantity of a material injected and its peak area was established by the analysis of synthetic mixtures. Yields (mol %) so determined were reproducible to within ±5% of the values quoted except that, for yields of less than 2%, the reproducibility decreased until, for yields of *ca.* 0·1%, it was within the range ±10%. Compounds were identified by comparison of their retention times with those of authentic materials on the two columns together with comparison of their mass spectra, obtained by combined g.l.c.–mass spectrometry, with those of authentic materials. Preparative gas chromatography was carried out on an F. and M. Prepmaster Junior 776 instrument. M.p.s were determined on a Kofler microhot-stage apparatus.

Materials. Acetic acid, benzene, and toluene were Fisons analytical reagents. Trifluoroacetic acid (B.D.H. laboratory reagent) was redistilled if it showed any discolouration. Trichloroacetic acid, anisole (pure by g.l.c.), and chlorobenzene (redistilled) were Fisons laboratory reagents. Lead tetra-acetate (B.D.H. laboratory reagent) was recrystallised from acetic acid and sucked dry at the pump. In most cases, residual acetic acid was not removed; iodometric titration showed that the solid contained 90% of lead tetra-acetate, and allowance was made for this when the material was weighed. For the experiments reported in Tables 2, 3, and 9, the recrystallised material was dried in a desiccator (2 mmHg) for 2 h over potassium hydroxide pellets; iodometric titration showed that the solid contained 96% of lead tetra-acetate.

m-Deuterioanisole was prepared by dropwise addition of 99·7% deuterium oxide (18 ml), with use of a 5 ml syringe and a septum cap, to the Grignard reagent from *m*-bromoanisole (50 g) and magnesium (7 g) in ether under nitrogen. After being set aside overnight under dry nitrogen, the solution was treated with solid carbon dioxide to remove unchanged Grignard reagent and was poured into dilute hydrochloric acid (500 ml). The ether extract was washed with 2M-sodium hydroxide solution and with water, dried ($MgSO_4$), and distilled to give *m*-deuterioanisole (19 g), b.p. 153—155° (lit.,[13] 155° for anisole). The content of unlabelled anisole was determined as 11·8% (mean of 15 scans) from the relative heights of the m/e 107, 108, and 109 ions in the mass spectrum.

Reference Compounds.—Phenyl trifluoroacetate was prepared by heating trifluoroacetic acid (18·3 g) and triphenyl phosphite (54·4 g) under reflux for 2 h and b.p. 146—149° (lit.,[14] 146·5—147°; lit.,[15] 149°). Phenyl trichloroacetate was prepared by heating trichloroacetic acid (16·3 g) and triphenyl phosphite (34 g) under reflux for 3 h. Distillation gave material, b.p. 90—100° at 1·5 mmHg, which was shown by g.l.c. combined with mass spectrometry to contain phenyl trichloroacetate as the major component (lit.,[15] b.p. 254—255°, 90·5—91° at 1·5 mmHg) and phenyl dichloroacetate as the minor component (lit.,[15] b.p. 247·5°). Benzyl trifluoroacetate was prepared by mixing benzyl alcohol (10·1 ml) with trifluoroacetic acid (8·3 ml) at room temperature. Heat was evolved, and after 1 h the product was fractionated to give the ester, b.p. 172—173° (lit.,[16] 177—178°; lit.,[17] 173—174°); n.m.r. spectrum (neat liquid): τ 2·74 (5H, s, ArH) and 4·87 (2H, s, CH_2).

2,4′-Dimethylbiphenyl was prepared from *p*-toluidine and toluene following the method of Gomberg and Pernert.[18] The product was distilled *in vacuo* from the tarry residue and fractionated (5 in column packed with glass helices) to give a colourless product, b.p. 276° (lit.,[18] 273—276°) shown by g.l.c. (silicone oil; 200°) to contain less than 2% bi-*p*-tolyl; n.m.r. spectrum: τ 2·77 (8H, s, ArH), 7·63 (3H, s, Me), and 7·74 (3H, s, Me). Bi-*o*-tolyl and bi-*p*-tolyl[19] were available in this laboratory.

The photolysis of *p*-chlorotoluene (100 mg) in toluene (100 ml), with a medium-pressure lamp for 24 h, gave a product shown by a combination of g.l.c. and mass spectrometry to contain 2,4′-dimethylbiphenyl and bi-*p*-tolyl and an additional isomer the retention time of which was slightly less than that of bi-*p*-tolyl and which, from the mode of preparation, was probably 3,4′-dimethylbiphenyl.

Phenyl-*p*-tolylmethane was prepared by the reduction of 4-methylbenzophenone with lithium aluminium hydride

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[13] Heilbron and Bunbury's 'Dictionary of Organic Compounds,' 4th edn., Eyre and Spottiswoode, London, 1965.

[14] R. F. Clark and J. H. Simons, *J. Amer. Chem. Soc.*, 1953, **75**, 6305.

[15] A. C. Pierce and M. M. Joullié, *J. Org. Chem.*, 1962, **27**, 3968.

[16] E. J. Bourne, M. Stacey, J. C. Tatlow, and R. Worrall, *J. Chem. Soc.*, 1958, 3268.

[17] F. Weygand and E. Leising, *Chem. Ber.*, 1954, **87**, 248.

[18] M. Gomberg and J. C. Pernert, *J. Amer. Chem. Soc.*, 1926, **84**, 1372.

[19] J. R. Lindsay Smith and R. O. C. Norman, *J. Chem. Soc.*, 1963, 2897.

in the presence of aluminium trichloride, following the method of Brown and White,[20] and was distilled *in vacuo* as a pale yellow liquid, b.p. 143—145° at 13 mmHg (lit.,[21] 145·5—145·7 at 13·5 mmHg) which was homogeneous by g.l.c.; n.m.r. spectrum: τ 2·80 (4H, s, ArH), 2·93 (5H, s, ArH), 6·10 (2H, s, CH_2), and 7·75 (3H, s, Me).

2-Hydroxy-5-methylbenzaldehyde was prepared by heating a solution of *p*-cresol (6 g) in 10M-sodium hydroxide (50 ml) with chloroform (40 ml) for 2 h under reflux. After acidification and distillation in steam, the ether extract of the alkali-soluble material was evaporated and added to a saturated solution of sodium metabisulphite (50 ml). The resulting precipitate of the hydrogen sulphite addition compound was dissolved in 2M-hydrochloric acid (100 ml) and the ether extract was dried and evaporated to give white crystals of the aldehyde, m.p. 55—56° (from aqueous ethanol) (lit.,[22] 56°), n.m.r. spectrum: τ −0·87 (1H, s OH, exchanged in D_2O), 0·13 (1H, s, CHO), 2·50—3·25 (3H, m, ArH), and 7·70 (3H, s, Me). The alkali-insoluble products from this reaction were freed from resin by distillation under reduced pressure. Trituration of the resulting oil in light petroleum (b.p. 60—80°) gave white crystals of 4-dichloromethyl-4-methylcyclohexa-2,5-*dienone, m.p.* 55° (lit.,[22] 55°); n.m.r. spectrum: τ 3·08 (2H, d, CH), 3·67 (2H, d, CH), 4·28 (1H, s, $CHCl_2$), and 8·55 (3H, s, Me).

2,4′-Dimethoxybiphenyl was prepared from *p*-anisidine and anisole[23] and was separated from highly coloured material by chromatography on alumina with chloroform–benzene (1 : 19, v/v) as eluant; preparative gas chromatography gave white crystals, m.p. 68—70° (from ethanol) (lit.,[23] 70°); n.m.r. spectrum: τ 2·54—3·32 (8H, m, ArH) and 6·25 and 6·28 (6H, 2s, OMe). 2,2′- and 4,4′-Dimethoxybiphenyl were available in this laboratory. A mixture of 2,4′-, 3,4′-, and 4,4′-dimethoxybiphenyl was also obtained by the photolysis of *p*-iodoanisole (2·2 g) in anisole (250 ml) with a medium-pressure u.v. lamp for 24 h. The product was freed from iodine with sodium thiosulphate solution and excess of solvent was evaporated off. Combined g.l.c.–mass spectrometry showed the product to consist mainly of 2,4′-dimethoxybiphenyl, with a small amount of 4,4′-dimethoxybiphenyl and a larger amount of a third dimethoxybiphenyl which, from the method of preparation, was presumed to be 3,4′-dimethoxybiphenyl.

Bis-(*p*-methoxyphenyl)methane was prepared by the addition of 4,4′-dimethoxybenzophenone (4·2 g) in dry ether (100 ml) during 10 min to a stirred mixture of lithium aluminium hydride (1 g) and aluminium trichloride (7·9 g) in dry ether (25 ml). After the vigorous reaction was over, the mixture was heated under reflux for 1 h, cooled to 0°, and treated with methyl formate until no further reaction was apparent. The mixture was poured into 20% sulphuric acid (200 ml) and the ether extract was dried ($MgSO_4$) and evaporated. The white, flaky crystals of bis-(*p*-methoxyphenyl)methane had m.p. 51—52° (from methanol) (lit.,[13] 52°); n.m.r. spectrum (CCl_4): τ 3·02 (4H, d, *J* 9 Hz, ArH), 3·33 (4H, d, *J* 9 Hz, ArH), 6·22 (2H, s, CH_2), and 6·31 (6H, s, OMe).

o-*Methoxyphenyl*-(p-*methoxyphenyl*)*methane*. Powdered aluminium trichloride (17 g) was added slowly, with shaking, to a mixture of anisole (70 ml) and *o*-methoxybenzoyl chloride (20 g). The mixture was heated under reflux for 1 h and then poured on to crushed ice (200 g) and concentrated hydrochloric acid (100 ml). The ether extract was washed with sodium hydrogen carbonate solution and with water and was dried ($MgSO_4$). Evaporation left an oil which, on addition of ethanol and cooling, gave bright yellow crystals of 2-*hydroxy*-4-*methoxybenzophenone* (14 g), m.p. 52—53° (from ethanol); n.m.r. spectrum (CCl_4): τ −1·95 (1H, s, OH, exchanged in D_2O), 2·15—3·30 (8H, m, ArH), and 6·20 (3H, s, OMe) (the aromatic multiplet included a pair of doublets centred at τ 2·39 and 3·12, *J* 9 Hz, from the *para*-substituted ring); mass spectrum: *m/e* 228 (M^+, 49%), 213 (4·7, *M* − Me), 197 (5·7, *M* − OMe), 135 (36, $MeO{\cdot}C_6H_4{\cdot}CO$), 121 (19, $HO{\cdot}C_6H_4{\cdot}CO$), 120 (25, $C_7H_4O_2$), 108 (100, C_7H_8O), 107 (4·4, $MeO{\cdot}C_6H_4$), and 93 (7·9, $HO{\cdot}C_6H_4$), *m** 51·2 (228 → 108), 71·5 (121 → 93), 84·9 (135 → 107), and 341 (114 → 197, $M^{2+} \rightarrow M^+ -$ OMe) (Found: C, 73·5 H, 5·1. $C_{14}H_{12}O_3$ requires C, 73·7; H, 5·3%).

Reduction of 2-hydroxy-4-methoxybenzophenone (6·2 g) with lithium aluminium hydride (1·5 g) and aluminium trichloride (12 g) was carried out as described for 4,4′-dimethoxybenzophenone. The resulting orange-red oil was dissolved in 10% potassium hydroxide solution (15 ml) and cooled in an ice bath. Dimethyl sulphate (3 ml) was added dropwise to the stirred solution. Stirring was continued for 1·5 h at 0° and then for a further 2 h on a boiling water bath. After being cooled to room temperature the dark syrupy liquid was washed with water, dilute hydrochloric acid, and again with water. The volatile components of the syrup were separated from resinous material by distillation at 1 mmHg pressure, and white crystals were obtained from the distillate by cooling in a methanol–dry ice bath. The crystals melted at room temperature to give a pale oil which produced only one peak on g.l.c. (silicone oil; 200°) and was identified as *o*-methoxyphenyl-(*p*-methoxyphenyl)methane (lit.,[13] m.p. 26°) by its n.m.r. spectrum [τ 2·66—3·37 (8H, m, ArH), 6·12 (2H, s, CH_2), and 6·28 and 6·34 (6H, 2s, OMe)] and its mass spectrum [*m/e* 228, M^+, 100%, 213 (16, *M* − Me), 197 (32, *M* − OMe), 121 (29, $MeO{\cdot}C_6H_4{\cdot}CH_2$), 91 (21, C_7H_7), and 77 (14, C_6H_5), *m** 199 (228 → 213) and 170·2 (228 → 197)].

Oxidations.—(i) *Benzene in trifluoroacetic acid*. A typical procedure for the experiments recorded in Table 1 was as follows. A solution of benzene (22·5 g) and lead tetra-acetate (3·8 g) in trifluoroacetic acid (19·7 g) was stirred for 24 h at room temperature. Phenyl trifluoroacetate and acetic acid were identified by combined g.l.c.–mass spectrometry (diethylene glycol adipate; 180°). The product was poured into water (200 ml) and the ether extract (2 × 250 ml) was shaken with M-sodium hydroxide (300 ml) for 10 min. After acidification with 2M-hydrochloric acid, the solution was neutralised with sodium hydrogen carbonate. The ether solution and the ether extract of the aqueous solution were combined, dried ($MgSO_4$), and evaporated to *ca.* 50 ml. The product was analysed by g.l.c. and mass spectrometry; the quantitative determination of phenol, phenyl acetate, and biphenyl was on the diethylene glycol adipate column (180°) with bibenzyl as internal standard.

For experiments recorded in Table 2 the procedure was as follows. A solution of lead tetra-acetate (2·587 g) in trifluoroacetic acid was made up to 100 ml in a graduated

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[20] B. R. Brown and A. M. S. White, *J. Chem. Soc.*, 1957, 3755.

[21] Beilstein's Handbuch, Band 5, I, 286.

[22] K. Auwers and F. Winternitz, *Ber.*, 1902, **35**, 465.

[23] W. J. Dunstan and G. K. Hughes, *J. Proc. Roy. Soc. New South Wales*, 1947, **80**, 77.

flask. Aliquot portions (10 ml) were pipetted into conical flasks and a measured volume of acetic acid was added. Benzene (10 ml) was then added with stirring, and after 36 h the solutions were worked up and analysed as before. The rate of darkening of the solution was much slower in the presence of acetic acid; the final colour varied from orange-red (no acetic acid) to yellow (2·2 ml of acetic acid), the darkest being the mixture which contained 0·6 ml of acetic acid.

For the experiments recorded in Table 3, the procedure was as follows. A solution of lead tetra-acetate (8·008 g) in trifluoroacetic acid was made up to 200 ml in a graduated flask. Aliquot portions (10 ml) were pipetted into conical flasks and a measured volume of benzene was added to each. The solutions were stirred for 1 h and after a further 24 h were worked up and analysed as just described. The final colour of the solution varied from dark red (2 or 5 ml of benzene) to pale yellow (100 ml of benzene).

(ii) *Benzene in trichloroacetic acid.* A typical procedure was as follows. Benzene (31·4 g), lead tetra-acetate (5·4 g), and trichloroacetic acid (29·6 g) were heated for 24 h at 75°. The solution was poured into 4M-sodium hydroxide solution (100 ml) and heated under reflux for 30 min on a boiling water bath. It was made acid again with 2M-hydrochloric acid and the ether extract was washed with sodium hydrogen carbonate solution. After drying (Na_2SO_4) and evaporation of the solvent, the product was analysed by g.l.c. and mass spectrometry. Quantitative determination of phenol and biphenyl was carried out as before. Phenyl trichloroacetate and small amounts of phenyl dichloroacetate and phenyl acetate were identified by analysis of the products of a similar reaction which was worked up with sodium hydrogen carbonate solution (which does not effect hydrolysis of these esters at a significant rate).

(iii) *Chlorobenzene in trifluoroacetic acid.* Chlorobenzene (1·2 g) and lead tetra-acetate (3·9 g) in trifluoroacetic acid (18·0 g) were heated for 4 h at 80°. The solution was poured into water and worked up and analysed as in (i); *p*-chlorophenol was determined on the diethylene glycol adipate column (190°) with phenyl benzoate as internal standard.

(iv) *Benzene and chlorobenzene in trifluoroacetic acid.* A typical experiment was as follows. Benzene (0·956 g), chlorobenzene (1·380 g), and lead tetra-acetate (1·61 g) in trifluoroacetic acid (12·7 g) were stirred for 24 h at room temperature. The solution was poured into water and the ether extract was shaken vigorously with sodium hydrogen carbonate solution until effervescence had ceased. After being dried (Na_2SO_4), the ether solution was added to toluene (1·295 g) and the amounts of unchanged benzene and chlorobenzene were determined by g.l.c. (silicone oil; 55°).

(v) *Large excess of benzene and chlorobenzene in trifluoroacetic acid.* A mixture of benzene (115·6 g) and chlorobenzene (166·3 g) was used. The procedure for the experiments recorded in Table 9 was as for those in Table 2 except that 20 ml of the benzene–chlorobenzene mixture was used in place of benzene. The mixtures were worked up after 48 h as in (i) and quantitative analysis was on the diethylene glycol adipate column (180°) with phenyl benzoate as internal standard. The rate of darkening of the solutions decreased in the presence of acetic acid; the final colour varied from orange-red to pale yellow, the darkest solution being that with 0·5 ml of acetic acid.

(vi) *Toluene in trifluoroacetic acid.* In experiment 1, toluene (1·80 g) was added to a solution of lead tetra-acetate (1·68 g) in trifluoroacetic acid (9·17 g). Heat was evolved, and the solution changed from yellow-green to dark purple within 30 s. After the solution had been stirred for 3 h and then poured into water, the ether extract was shaken with 2M-sodium hydroxide, acidified with dilute hydrochloric acid, and neutralised with sodium hydrogen carbonate solution. After drying (Na_2SO_4), evaporation of the solvent left a dark oil which was analysed by g.l.c. and mass spectrometry. Quantitative analysis of the cresols and cresyl acetates was on the silicone column at 140° with naphthalene as internal standard; that of the bitolyls and phenyl-*p*-tolylmethane was on the silicone column at 200° with biphenyl as internal standard. A typical procedure for experiments 2—4 was as follows. A solution of lead tetra-acetate (4·73 g) in trifluoroacetic acid (21·2 g) was added dropwise during 2 h to toluene (20·7 g) at 0°, with stirring. Stirring was continued for a further 3 h, and the solution was worked up and analysed as in experiment 1. In one experiment, *m*- and *p*-cresol were analysed separately at 135° on a column prepared from tritolyl phosphite, Bentone 34, and Celite (1 : 1 : 8, w/w).

(vii) *Toluene in trichloroacetic acid.* Toluene (100 ml) was added to a mixture of lead tetra-acetate (12·78 g) and trichloroacetic acid (40·6 g). The solids dissolved on shaking to give an orange solution which turned yellow during 30 min. After 24 h, the solution was orange and no precipitation had occurred, but after being heated for 9 days at 50° a small quantity of a lead(II) salt had been precipitated from the dark brown solution. The product was poured into 4M-sodium hydroxide (250 ml) and heated under reflux for 2 h with frequent shaking. After acidification with 2M-hydrochloric acid, the ether extract was washed with sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaporated. The residue was analysed by g.l.c.–mass spectrometry. Quantitative analysis of cresols, cresyl acetates, and bitolyls was as in (vi), experiment 1, and that of 2-hydroxy-5-methylbenzaldehyde and 4-dichloromethyl-4-methylcyclohexa-2,5-dienone was on the diethylene glycol adipate column (185°); biphenyl was the internal standard in each case.

(viii) *Anisole in trifluoroacetic acid.* (a) Anisole (22 g) was added dropwise during 2 h to a stirred solution of lead tetra-acetate (4·94 g) in trifluoroacetic acid (32·9 g) at 0°. The first few drops of anisole produced an intense green colouration and momentarily a temperature rise of *ca.* 20°. After addition of *ca.* 2 ml the solution was very dark and further addition of anisole had little observable effect. After completion of the addition the solution was stirred for a further 3 h and then poured into water. The ether extract was shaken with sodium hydrogen carbonate solution until effervescence ceased and then dried (Na_2SO_4). Evaporation left a very dark oil which was analysed by g.l.c. and mass spectrometry. Quantitative analysis of *p*-methoxyphenol and the dimethoxybiphenyls was on the diethylene glycol adipate (180°) and the silicone oil column (200°), respectively, with bibenzyl as internal standard.

(b) A solution of lead tetra-acetate (4·84 g) in trifluoroacetic acid (18·66 g) was added dropwise during 2 h to anisole (22·6 g) stirred at 0°. There was no appreciable temperature rise and the solution remained an intense green colour throughout the addition. When the oxidant solution had been added, stirring was continued for 3 h and the solution was then worked up and analysed as in (a). (In one reaction, left overnight, white needles formed in the solution. The crystals were very sensitive to moisture and could not be purified; they contained lead(II) and may have been lead bistrifluoroacetate.)

(c) A solution of lead tetra-acetate (6·67 g) in trifluoroacetic acid (21·2 g) was added dropwise during 2 h to a stirred mixture of benzene (31·0 g) and anisole (42·1 g) at 0°. After being stirred for a further 3 h, the solution was worked up and analysed as in (a).

(d) A typical procedure for the experiments recorded in Table 7 was as follows. A solution of lead tetra-acetate (3·66 g) in trifluoroacetic acid (15·0 g) and acetic acid (1·216 g) was added dropwise during 2 h to a stirred sample (55 g) at 0° of a mixture of benzene (151·9 g) and anisole (209·3 g). Stirring was continued for 12 h at room temperature and the product was worked up as in (viii) (a). Quantitative analysis of dimethoxybiphenyls, bis(methoxyphenyl)methanes, 4-methoxybiphenyl, and *p*-methoxyphenyl acetate was on the silicone oil column (200°) with biphenyl as internal standard.

(ix) *Anisole in trichloroacetic acid.* A typical procedure was as follows. Anisole (54·0 g) was added to a mixture of lead tetra-acetate (6·70 g) and trichloroacetic acid (14·0 g). A blue-green colour appeared immediately and the solid gradually dissolved. The solution became very dark within a few min and, after it had been stirred for 2 h, a white flocculent precipitate began to form. Precipitation appeared to be complete after the solution had been stirred for 72 h. The precipitate was washed with anisole until it was colourless, dried *in vacuo* to give *bis*-p-*methoxyphenyllead bistrichloroacetate* (characterised further later), and recrystallised from benzene before microanalysis; n.m.r. spectrum (acetone): τ 2·03 (4H, d, ArH), 2·80 (4H, d, ArH), and 6·15 (6H, s, OMe) (Found: C, 31·9; H, 2·3; Cl, 26·9; Pb, 26·2. $C_{18}H_{14}Cl_6O_6Pb$ requires C, 29·0; H, 1·9; Cl, 28·5; Pb, 27·7%). The filtrate was poured into 4M-sodium hydroxide (50 ml) and heated for 30 min on a boiling water bath. The solution was made acid again with 2M-hydrochloric acid and the ether extract was washed with sodium hydrogen carbonate solution. After drying (Na_2SO_4) and evaporation of the solvent, the product was analysed by gas chromatography and mass spectrometry; dimethoxybiphenyls and methoxyphenols were determined on the silicone oil column (200°) and the diethylene glycol adipate column (180°), respectively, with bibenzyl as internal standard.

In another experiment, a mixture of anisole (125 g) and benzene (90 g) was added to lead tetra-acetate (31 g) and trichloroacetic acid (60 g). After being stirred for 72 h, the solution was worked up and analysed as already described.

The Lead Compound (I).—(i) The proportion of methoxy-protons was determined as follows. A sample of the compound (I) (0·0422 g), recrystallised from benzene, and bibenzyl (0·0183 g) were dissolved in dichloromethane (5 ml) containing a few drops of [$^2H_6$]dimethyl sulphoxide. The singlets in the n.m.r. spectrum at τ 6·19 (OMe) and 7·10 (CH_2) were integrated, and from the ratio of the peak areas (mean of several scans) the proportion of methoxy-protons per g of (I) was calculated. A similar determination with material which had not been recrystallised suggested that another methoxy-containing compound, probably anisole, was occluded in the solid.

(ii) *Iododeplumbylation.* A suspension of the compound (I) (0·336 g) and iodine (1·0 g) in benzene (50 ml) was stirred for 12 h. The product was poured into water and the ether extract was washed with excess of sodium metabisulphite solution and dried ($MgSO_4$). The yield of *p*-iodoanisole was determined by g.l.c. (silicone oil column; 180°) with bibenzyl as internal standard.

(iii) Trifluoroacetic acid (30 g) was added with stirring to compound (I) (1·163 g). The solid dissolved rapidly and the green solution rapidly darkened. After being set aside overnight, the product was poured into water and the ether extract was washed with sodium hydrogen carbonate solution and dried ($MgSO_4$). After evaporation of excess ether, the product was analysed by g.l.c. and mass spectrometry. The diethylene glycol adipate column was used for quantitative analysis of anisole (120°; *p*-cymene as internal standard) and *p*-methoxyphenol (180°; bibenzyl as internal standard), and the silicone oil column was used likewise for the dimethoxybiphenyls (200°; bibenzyl as internal standard).

(iv) A typical procedure for the experiments in Table 5 was as follows. Trifluoroacetic acid (15·3 g) was added to a stirred suspension of compound (I) (0·2256 g) in anisole (17·64 g). The solid rapidly dissolved and the red solution was worked up after 24 h. Quantitative analysis of the dimethoxybiphenyls was as in (iii). The procedure for the experiments in Table 6 was the same but with an equimolar mixture of anisole and benzene in place of anisole.

(v) *Deuterium-labelling studies.* Trifluoroacetic acid (15 g) was added to a stirred suspension of the compound (I) (0·1557 g) in *m*-deuterioanisole (the sample of which contained 12% of unlabelled material). The product was worked up after 24 h and analysed by g.l.c.–mass spectrometry (silicone oil column; 200°); the proportions of each of 2,2′-, 2,4′-, and 4,4′-dimethoxybiphenyl containing none, one, or two deuterium atoms were determined from the relative heights of the ions with *m/e* 213, 214, 215, and 216.

Electronic Absorption Spectra of Dimethoxybiphenyl Radical-cations.—The green solution from addition of lead tetra-acetate to anisole and trifluoroacetic acid in dichloromethane had $\lambda_{max.}$ 428 and *ca.* 750 nm (broad), neither of which corresponds to the individual components. The same spectrum was observed when lead tetra-acetate was added to 4,4′-dimethoxybiphenyl and trifluoroacetic acid in dichloromethane. With 2,4′- instead of 4,4′-dimethoxybiphenyl, the spectrum was different [$\lambda_{max.}$ 411 and *ca.* 650 nm (broad)], but addition of 4,4′-dimethoxybiphenyl to this solution restored the original spectrum.

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