936. *Reactions of Lead Tetra-acetate. Part I. Reactions with Some Benzenoid Compounds.*

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The reactions of lead tetra-acetate with benzene, toluene, anisole, and nitrobenzene have been investigated and their mechanisms are discussed. At about 120°, methylation occurs through the free methyl radical, but at $<80°$ there is no evidence for the participation of radicals in the initial reaction between lead tetra-acetate and the aromatic compounds. The acetoxylation of anisole at 80° is an electrophilic process, and the biphenyl derivatives that are also formed when this reaction is carried out in an aromatic solvent are derived by homolysis of another product, *p*-methoxyphenyl-lead triacetate, followed by reaction of the resulting aryl radicals with the solvent. Results for the electrolytic acetoxylation of anisole and toluene are reported.

DESPITE many investigations of the reactions of benzenoid compounds with lead tetra-acetate, the mechanisms of these processes are not fully understood, and some conflicting theories are current in the literature. The following examples provide the background to the reactions we have investigated.

(*a*) Many benzenoid compounds have been methylated by treatment with lead tetra-acetate in refluxing acetic acid.[1,2] Quantitative studies of the isomer distribution of the products have been reported only for chlorobenzene and ethyl benzoate, and the results [2] are consistent with the view that radicals are formed under these conditions,[3] but it has been argued on two grounds that the radical responsible for methylation cannot be the free methyl radical.[2] First, the ratios of the three chlorotoluenes formed from chloro-benzene differ from those obtained by methylation with two other sources of the methyl radical, namely, di-t-butyl peroxide [4] and methylmercuric iodide [5] (which give the same ratios within experimental error). In particular, a higher proportion of the *para*-substituted compound is obtained with lead tetra-acetate (19%, compared with 11 [4] and 10% [5]), and this has been ascribed to the radical's having a degree of electrophilic character. Secondly, the methyl radical would be expected to react with the toluenes formed to give benzyl radicals, and hence bibenzyls by dimerisation, but such products have not been isolated. It has therefore been suggested that the methyl radical from lead tetra-acetate is complexed with lead, and that in this form it is more electrophilic than the free radical.[2] On the other hand, the phenylation of nitrobenzene and pyridine with lead tetrabenzoate gives the corresponding phenylated derivatives in relative amounts closely similar to those obtained with other sources of the phenyl radical,[6] so that in this case the free phenyl radical is clearly involved.

(*b*) Toluene is oxidised by lead tetra-acetate at 80° to give mainly benzyl acetate. Mediation of benzyl radicals has been postulated,[7] but the absence of bibenzyl as a product [2,8] has led to the conclusion that free benzyl radicals are not present. The suggestion that a " complex intermediate " is formed and decomposes to benzyl acetate [8] has recently been elaborated by Davies, who has suggested that reaction occurs through two cyclic transition states, without the mediation of free radicals, as follows: [2]
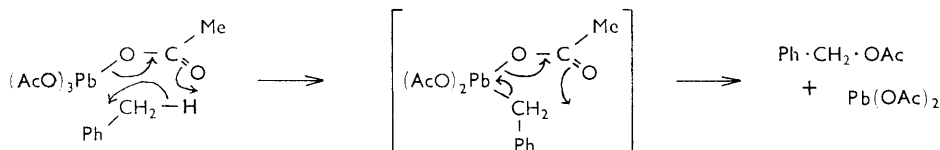
(*c*) Many polynuclear aromatic hydrocarbons are acetoxylated by lead tetra-acetate at room temperature,[9] but in the benzene series acetoxylation occurs only with anisole and related phenyl ethers, and then only on heating.[10] For example, anisole reacts at 80° to give the *p*-acetoxy-derivative, together with very small quantities of products suggestive of attack by the *p*-methoxyphenyl radical on the solvent (*e.g.*, 4-methoxy-4′-nitro-biphenyl is formed in nitrobenzene). These results have been interpreted in terms of free-radical intermediates, *p*-acetoxyanisole being thought to arise from the union of the *p*-methoxyphenyl and the acetoxy-radical,[10] and recent studies have led to the conclusion that the reaction is homolytic.[11] However, this mechanism is *a priori* unlikely, since free radicals normally react with benzenenoid compounds by addition to the nucleus rather than by abstracting hydrogen from it, and this is true even when the bond that would be formed by abstraction is as strong as the O–H bond in water; [12,13] the formation of

1 Fieser, Clapp, and Daudt, *J. Amer. Chem. Soc.*, 1942, **64**, 2052.
2 Davies, *J.*, 1963, 2351.
3 Kharasch, Friedlander, and Urry, *J. Org. Chem.*, 1951, **16**, 533.
4 Cowley, Norman, and Waters, *J.*, 1959, 1799.
5 Corbett and Williams, *Proc. Chem. Soc.*, 1961, 240.
6 Hey, Stirling, and Williams, *J.*, 1954, 2747; 1955, 3963.
7 Detilleux and Jadot, *Bull. Soc. roy. Sci. Liège*, 1955, 366.
8 Cavill and Solomon, *J.*, 1954, 3943.
9 Fieser and Putnam, *J. Amer. Chem. Soc.*, 1947, **69**, 1041.
10 Cavill and Solomon, *J.*, 1955, 1404.
11 Jadot and Neuray, *Bull. Soc. roy. Sci. Liège*, 1960, 138.
12 Dixon and Norman, *Proc. Chem. Soc.*, 1963, 97.
13 Lindsay Smith and Norman, *J.*, 1963, 2897.

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the *p*-methoxyphenyl radical would therefore not be expected. Moreover, monosubstituted benzenes usually react with radicals to give all three nuclear-substituted products, in most cases with predominance of the *ortho*-derivative, so that *ortho*- and *meta*-acetoxylated compounds would be expected from anisole.

An entirely different mechanism has been proposed for the reaction of a related compound, resorcinol dimethyl ether, with lead tetra-acetate.[14] Reaction in benzene at 80° gives the organo-lead compound (I) which, on being heated in acetic acid, gives mainly resorcinol dimethyl ether, but also some of the acetoxylated product (III) together with minor products. It has been suggested that the compound (I) dissociates heterolytically to give (II) and thence (III): [14]

OMe — OMe — OMe
Pb(OAc)₃ (I) — (II) + Pb(OAc)₃⁻ — OAc (III)
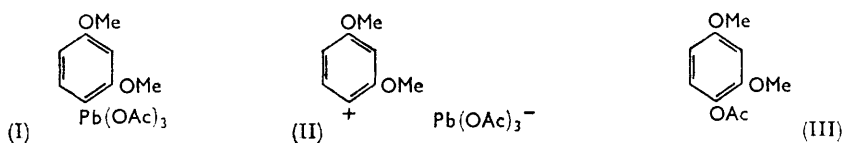
The formation of anisole alone when *p*-methoxyphenyl-lead triacetate is heated in acetic acid [15] appears to exclude an analogous mechanism for the acetoxylation of anisole, at least in this solvent.

The work described in this Paper was carried out in the hope that a clear distinction could be made between the alternative ionic and free-radical pathways in these reactions.

RESULTS

Reactions of Benzene, Toluene, Nitrobenzene, and Anisole with Lead Tetra-acetate.—These reactions were studied in acetic acid at 25, 80°, and at reflux temperature. None reacted at 25°.

No products were detected from the reaction of benzene at 80°, but at the reflux temperature reaction occurred and gave both some toluene and the same products as toluene under these conditions. Phenyl acetate was not formed.

Toluene reacted at 80° to give benzyl acetate and benzaldehyde, the former in greater yield, but neither nuclear acetoxylated nor nuclear methylated products were detected. At the reflux temperature, three further products, *o*- and *p*-methylbenzyl acetate and *o*-tolualdehyde, were formed, the second of these in smaller quantity than the others, but neither bibenzyl nor stilbene were detected. Two unidentified products were found from the oxidation of bibenzyl at the reflux temperature, and when a mixture of bibenzyl and benzene in ∼1 : 10 mole ratio was similarly oxidised for one hour, about 85% of the bibenzyl was consumed, of which only about 20% could be accounted for as the two unidentified products.

Nitrobenzene reacted only at the reflux temperature, giving the three nitrotoluenes in the relative proportions, expressed as percentages: *o*-, 72·9; *m*-, 3·7; *p*-, 23·4. No products of nuclear acetoxylation could be detected.

Anisole gave *o*- and *p*-acetoxyanisole at 80°, neither the *meta*-isomer nor methylated products being detected. Acetoxylation also occurred in benzene and anisole, the relative proportions of *ortho*- and *para*-derivatives in the three solvents being: acetic acid, 18·8 : 81·2; benzene, 33·3 : 66·7; anisole, 35·1 : 64·9. In each solvent, a small amount of phenyl acetate was formed and, in benzene, 4-methoxybiphenyl was also detected. More than 15 times as much *p*-acetoxyanisole was formed in acetic acid as in benzene when reactions were carried out under otherwise identical conditions.

p-Methoxyphenyl-lead triacetate was isolated from the reaction of anisole with lead tetra-acetate both in benzene and in acetic acid at 80°, a higher yield being obtained in the

[14] Preuss and Janshen, *Arch. Pharm.*, 1960, **293**, 933; 1962, **295**, 284.
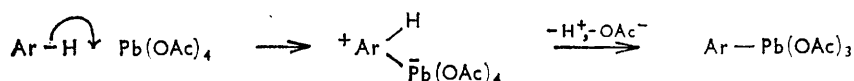[15] Criegee, Dimroth, and Schempf, *Chem. Ber.*, 1957, **90**, 1337.

latter solvent. Attempts to isolate the corresponding lead compounds from benzene and toluene in acetic acid at 80° were unsuccessful.

Decomposition of *p*-methoxyphenyl-lead triacetate in anisole, benzene, or acetic acid at 80° gave no *p*-acetoxyanisole. The only products detected and identified were anisole when acetic acid was the solvent, and 4-methoxybiphenyl when benzene was the solvent. A similar decomposition of phenyl-lead triacetate in anisole gave the three methoxybiphenyls in the relative proportions: *o*-, 68·5; *m*-, 19·1; *p*-, 12·4.

Electrolytic Studies.—Saturated solutions of potassium acetate in acetic acid were electrolysed in the presence of toluene, anisole, and nitrobenzene. Both toluene and anisole gave acetoxylated products, the isomer distributions being, for toluene: *o*-, 47·7; *m*-, 11·2; *p*-, 41·1%; and for anisole: *o*-, 69·9; *m*-, 1·8; *p*-, 28·3%. Methylated products were detected, in traces only, with nitrobenzene, the *ortho*-derivative predominating.

DISCUSSION

Formation and Decomposition of Organo-lead Compounds.—Anisole and resorcinol dimethyl ether react with lead tetra-acetate to give aryl-lead triacetates at those nuclear positions that are most strongly activated towards electrophilic reagents, and this fact, coupled with the failure of benzene and toluene (which are much less reactive towards electrophiles) to give analogous products, suggests that lead tetra-acetate here reacts as an electrophile. This may reasonably be associated with the ability of lead to expand its valence octet, and of acetate ion to be displaced from the resulting complex:

$$\text{Ar--H} \; \text{Pb(OAc)}_4 \longrightarrow {}^{+}\text{Ar} \diagdown \begin{matrix} \text{H} \\ \text{Pb(OAc)}_4 \end{matrix} \xrightarrow{-\text{H}^{+},-\text{OAc}^{-}} \text{Ar--Pb(OAc)}_3$$

Two other nuclear metallations of this type are already known: mercuration is well established as an electrophilic process,[16,17] while the pattern of substitution products in thallilation with thallium tri-isobutyrate [18] suggests that this is also an electrophilic reaction.

That only the *para*-substituted lead derivative could be isolated from anisole is compatible with such a mechanism, for electrophilic substitutions in anisole give barely detectable quantities of the *meta*-derivative, together with low *ortho* : *para* ratios in most instances even when the reagent does not have a large steric requirement.[19] Moreover, there may be steric hindrance to *ortho*-substitution by the lead atom of lead tetra-acetate. Finally, in an analogous reaction, the mercuration of anisole with mercuric acetate in acetic acid at 25°, the *ortho* : *para* ratio [17] is only 14 : 86.

The nature of the products derived from the decomposition of *p*-methoxyphenyl-lead triacetate is clearly determined by the nature of the solvent. The formation of anisole in acetic acid probably occurs by a pathway analogous to that in the acid-catalysed proto-deplumbylation of aryltrialkylplumbanes,[20] *i.e.*, essentially by the reversal of the reaction leading to the production of the organo-lead compound. The formation of 4-methoxybiphenyl in benene is suggestive of the formation of the *p*-methoxyphenyl radical by homolytic fission of the lead–carbon bond, and this view is supported by our finding that the isomer distribution of methoxybiphenyls resulting from the decomposition of phenyl-lead triacetate in anisole at 80° is similar to that (*o* : *m* : *p* = 67 : 18 : 15) obtained at 100° from the reaction of anisole with the phenyl radical derived from dibenzoyl peroxide.[21]

[16] Schramm, Klapproth, and Westheimer, *J. Phys. Colloid Chem.*, 1951, **55**, 843; Brown and McGary, *J. Amer. Chem. Soc.*, 1955, **77**, 2300, 2306, 2310.

[17] Brown and Goldman, *J. Amer. Chem. Soc.*, 1962, **84**, 1650.

[18] Glushkova and Kocheshkov, *Izvest. Akad. Nauk S.S.S.R., Otdel khim. Nauk*, 1957, 1186; *Doklady Akad. Nauk S.S.S.R.*, 1957, **116**, 233.

[19] Norman and Radda, *J.*, 1961, 3610.

[20] Eaborn and Pande, *J.*, 1961, 3715.

[21] Suehiro, *J. Chem. Soc. Japan*, 1951, **72**, 301 (*Chem. Abs.*, 1952, **46**, 2522).

The absence of *p*-acetoxyanisole as a product of these decompositions (in agreement, in the case of the acetic acid solvent, with a previous report [15]) indicates that acetoxylation does not occur through the organo-lead compound. It is possible that the products isolated by Preuss and Janshen from the decomposition of 2,4-dimethoxyphenyl-lead triacetate in boiling acetic acid [14] arise from further reactions of the main products, resorcinol dimethyl ether and lead tetra-acetate.

Nuclear Acetoxylation.—The view that the *para*-acetoxylation of anisole by lead tetra-acetate involves the union of two free radicals was based on the fact that biphenyl derivatives, products characteristic of radical reactions, accompany the acetoxylation.[10] We have shown that biphenyls can be formed as a result of the homolytic decomposition of an organo-lead intermediate, and that this decomposition does not lead to nuclear acetoxylation; doubt is thus cast on the supposition that nuclear acetoxylation is a homolytic process. It is therefore pertinent to re-examine the facts available about this reaction.

First, anisole gives *o*- and *p*-acetoxyanisole at a temperature (80°) at which neither it nor the other monosubstituted benzenoid compounds that we examined undergoes methylation. The acetoxy-radical is known to decompose rapidly to the methyl radical and carbon dioxide,[22] so that if this were the radical responsible for acetoxylation, methylation would be expected as an accompanying reaction.

Secondly, enormous differences exist in the ease with which aromatic compounds undergo acetoxylation: polynuclear hydrocarbons react [9] at 25°, anisole does not, but reacts at 80°, while benzene, toluene, and nitrobenzene do not react in this way even at higher temperatures. The reactivities of these compounds towards free radicals hardly differ by large enough factors to account for the observed wide spread, even though the acetoxy-radical would be expected to show electrophilic characteristics similar to those of the hydroxyl radical,[23,24] and hence to be more selective than " neutral " radicals such as phenyl (*e.g.*, the relative reactivities of anisole and benzene towards ·OH are [23] about 6 : 1). Moreover, the rate of acetoxylation of anthracene is enormously increased by the addition of methanol,[9] which is not to be expected of a homolytic process but is consistent with the reaction's being heterolytic. Further, in many electrophilic substitutions, anisole and polynuclear hydrocarbons are more reactive than benzene or toluene by several powers of ten,[25] so that the failure to detect acetoxylated derivatives from benzene, toluene, and nitrobenzene would be understandable if the reagent were electrophilic.

Finally, the possibility that the acetoxylation of anisole occurs through the acetoxy-radical may be discounted, as a result of our finding that the isomer distribution of the derivatives is markedly different from that obtained by the electrolytic procedure, for which there is evidence that the acetoxy radical is involved (see below). However, the fact that the yield of acetoxylated product is far greater, after the same time, when reaction is carried out in acetic acid than in benzene is consistent with the occurrence of an ionic mechanism, for the more polar solvent should increase the rate of reaction when the transition state is more polar than the reactants. In addition, the low *ortho* : *para* ratios for the reactions of anisole are consistent with this view, whereas homolytic substitutions normally give high ratios [26] (*e.g.*, that for the free-radical hydroxylation of anisole [23] is 84 : 16). The lower ratio obtained in acetic acid than in benzene or anisole as solvent is possibly due to complexing between lead tetra-acetate and acetic acid,[27] as a result of which the electrophile has a different selectivity for steric or electronic reasons.

[22] Walling, " Free Radicals in Solution," John Wiley, New York, 1957, p. 493.
[23] Norman and Radda, *Proc. Chem. Soc.*, 1962, 138.
[24] Dixon, Norman, and Buley, *J.*, 1964, 3625.
[25] de la Mare and Ridd, " Aromatic Substitution," Butterworths Scientific Publications, London, 1959.
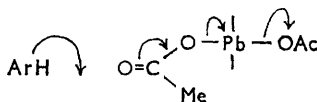[26] Walling, " Free Radicals in Solution," John Wiley, New York, 1957, p. 484.
[27] Benson, Sutcliffe, and Walkley, *J. Amer. Chem. Soc.*, 1959, **81**, 4488.

We therefore suggest that nuclear acetoxylation is an electrophilic process and occurs, on suitably activated aromatic compounds, as follows:
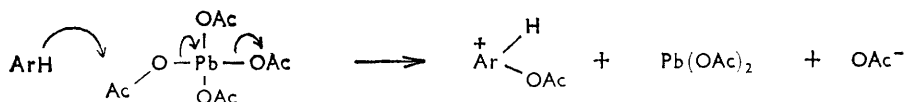
(It should be noted that displacement by the aromatic on the *carbonyl*-oxygen:

is at present an equally acceptable alternative.)   This mechanism has also been suggested recently for the first of a number of successive reactions in the oxidation of an indole with lead tetra-acetate.[28]

It therefore appears that lead tetra-acetate is an ambident electrophile, having the capacity to react at both the lead atom and at an oxygen of the acetate group.

Methylation.—Reference was made earlier to Davies's view that the methylation of benzenoid compounds by lead tetra-acetate at high temperatures occurs through a complexed, rather than a free, radical.   We do not find evidence for this interpretation in the present results.   First, nitrobenzene gives the nitrotoluenes in very similar proportions to those ($o : m : p = 65\cdot5 : 6 : 28\cdot5$) obtained when di-t-butyl peroxide is the source of the methyl radical.[4]   In particular, a complexed and electrophilic methyl radical would be expected to give a higher proportion of *m*-nitrotoluene than the free radical (cf. the higher proportion of *meta*-derivative formed in *p*-chloro- and *p*-bromo-phenylation than in phenylation of nitrobenzene [29]), whereas in practice the proportions are the same within the limits of accuracy of the measurement.   It should be noted that small differences in the selectivity of the radical are in any case to be expected, since the methylations compared by Davies [2] were conducted at different temperatures.[30]

Secondly, although the methyl radical would be expected to react with toluene to give the benzyl radical and hence bibenzyl, the failure to detect bibenzyl as a product does not necessarily imply that the methyl radical is complexed, as the following argument shows. The extent of formation of bibenzyl should not be large, because toluene undergoes both nuclear substitution and side-chain acetoxylation in the conditions in which methyl radicals are present, and moreover the benzyl radical might undergo other oxidations.   Our finding that bibenzyl is very largely consumed when oxidised with excess of lead tetra-acetate therefore suggests that, if bibenzyl were formed from toluene, it would react further and essentially completely.   Finally, bibenzyl has been found as a product of the photochemical reactions of both benzene and toluene with lead tetra-acetate,[31] and since, in these conditions, nuclear methylation and side-chain acetoxylation occur analogously to the thermal reactions at the reflux temperature in acetic acid, the processes are evidently closely similar in mechanism.

Benzyl acetate is formed from toluene in conditions (80°) in which there is no evidence for the presence of methyl or other radicals: thus, nuclear methylation does not occur at this temperature.   Evidently this side-chain acetoxylation occurs without the intermediation of the benzyl radical, and it is reasonable to accept the view that it takes place

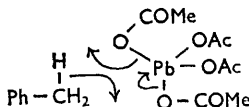[28] Chen and Leete, *Tetrahedron Letters*, 1963, 2013.
[29] Williams, " Homolytic Aromatic Substitution," Pergamon Press, 1960, p. 71.
[30] Kent and Norman, *J.*, 1959, 1724.
[31] Franzen and Edens, *Angew. Chem.*, 1961, **73**, 579.

through either the two cyclic transition states described above or the alternative one-step mechanism:

The acetoxylation of olefins at the allylic position [32] may occur by an analogous mechanism.

Electrolytic Acetoxylation.—The distributions of the isomers of the acetoxyanisoles and acetoxytoluenes obtained by the electrolytic method resemble those obtained in two well studied homolytic substitutions, phenylation [21,33] and methylation, [4,34] in that the *ortho*-derivative is the major product, but differs in that, as with homolytic hydroxylation, [13,23] the *para*-position is more reactive than the *meta*-position.* This suggests that the attacking entity is a radical with an electrophilic character, which is also consistent with the failure of nitrobenzene to undergo electrolytic acetoxylation. Such a character appears to be typical of oxy-radicals, for the benzoyloxylation of anisole, like the hydroxylation, [23] gives no *meta*-derivative, [36] while nitrobenzene gives a higher percentage of *meta*-derivative on benzoyloxylation [37] than when phenylated [33,37] or methylated. [4]

There is therefore strong evidence that the acetoxy-radical is involved in electrolytic acetoxylation. In the light of previous studies of the stability of the acetoxy-radical, it is surprising that homolytic acetoxylation rather than methylation is observed, but it must be remembered that reaction probably occurs on the surface of the electrode, [38] and that the acetoxy-radical may not become sufficiently free from this surface to undergo decomposition.

Conclusions.—The results of the present work together with those previously reported give no evidence for the participation of radicals in the *initial* reaction of lead tetra-acetate with benzenoid compounds, except at the high temperatures at which lead tetra-acetate itself undergoes homolysis to the methyl radical. In those processes for which there is positive evidence for the mediation of radicals, it is probable that these are derived from the homolysis of an initial product of an ionic reaction, as in the formation of biphenyls from anisole. As far as the initial reaction is concerned, our conclusion is similar to that reached for the diverse reactions of lead tetra-acetate with aliphatic compounds: that these are characterised by electrophilic attack on an electron-rich site in the organic molecule, followed by decomposition of the resulting intermediate. [32]

EXPERIMENTAL

Gas-chromatographic Analysis.—Gas chromatography was used both for (*a*) detecting the products of the reactions and (*b*) quantitative analysis of isomeric products.

(*a*) Products from lead tetra-acetate oxidations, with the exception of phenyl acetate, were collected from the column and identified by infrared spectroscopy. Evidence for the formation of phenyl acetate (from anisole at 80°) was derived from the identity of retention times of the product and authentic material on each of the columns 1 and 2, but the product was formed in too small a yield for isolation. Of the products from the electrolytic oxidations, *o*-tolyl acetate and *o*- and *p*-acetoxyanisole were identified by isolation and infrared spectroscopy; *m*- and *p*-tolyl acetates could not be resolved but were identified in the isolated mixture by infrared spectroscopy; *m*-acetoxyanisole was formed in too small an amount for collection, but was identified by infrared spectroscopy when material corresponding in retention times to it and its

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* The *ortho* : *para* ratio for anisole is similar to that reported for a previous electrolytic study by Hayashi and Wilson who found this ratio is 67—70 : 33—30, but did not detect the *meta*-derivative. [35]

[32] Criegee in " Neuere Methoden der Preparativen Organischen Chemie," Band II, ed. W. Foerst, Verlag Chemie, Heidelberg, 1961, p. 252.
[33] Williams, " Homolytic Aromatic Substitution," Pergamon Press, Oxford, 1960, p. 68.
[34] Eliel, Rabindran, and Wilen, *J. Org. Chem.*, 1957, **22**, 859.
[35] Hayashi and Wilson, 126th Amer. Chem. Soc. Meeting, New York, 1954, p. 78-O.
[36] Lynch and Moore, *Canad. J. Chem.*, 1962, **40**, 1461.
[37] Lynch and Pausacker, *Austral. J. Chem.*, 1957, **10**, 329.
[38] Conway and Dzieciuch, *Canad. J. Chem.*, 1963, **41**, 21.

para-isomer was collected. The extent of methylation from the electrolytic experiment with nitrobenzene was so small that isolation of products proved impossible, but analysis (column 1) gave small peaks corresponding to the three nitrotoluenes, that corresponding to the *ortho*-isomer being the largest.

(*b*) Product ratios were determined to within $\pm 3\%$ by the procedure described previously.[13] Synthetic mixtures of products were subjected to the appropriate extraction procedures to show that no product was lost preferentially.

Five columns (see Table) were employed, with nitrogen as carrier gas. A hydrogen-inject flame ionisation detector coupled to a Sunvic recorder gave a linear response. Entries under

Column no.	Coating material and inert support	Isomers separated	Temp.
1	2,4,7-Trinitrofluorenone (20% w/w) on 40—60 mesh " aqua regia-treated " firebrick	Nitrotoluenes	160°
2	Diethylene glycol adipate polyester (20% w/w) on " aqua regia-treated " firebrick	Acetoxyanisoles	180
3	Diethylene glycol adipate polyester (20% w/w) and phosphoric acid (2% w/w) on 60—100 mesh Embacel	Methoxybiphenyls	180
4	Tri-(2,4-xylyl) phosphate (5% w/w) on 60—100 mesh Embacel	Cresols	115
5	Apiezon " L " grease (10% w/w) on 100—120 mesh Celite		100

the heading " isomers separated " signifies that the *ortho*-, *meta*-, and *para*-isomers of the compounds concerned were fully resolved under the conditions quoted. Thus, the acetoxyanisoles and methoxybiphenyls (from the acetoxylation and phenylation of anisole) and the nitrotoluenes (from the methylation of nitrobenzene) were analysed as such. It was not possible to find a stationary phase that gave satisfactory resolution of *m*- and *p*-tolyl acetate (from the electrolytic acetoxylation of toluene), or one from which the nitrophenyl acetates (possible products from the acetoxylation of nitrobenzene) were eluted. The mixture of tolyl acetates was converted by alkaline hydrolysis into a mixture of cresols which was analysed on tri-(2,4-xylylene) phosphate,[39] and products from nitrobenzene were submitted to alkaline hydrolysis followed by methylation with diazomethane to give nitroanisoles, which could be chromatographed on 2,4,7-trinitrofluorenone.[40] It was shown, by submitting synthetic mixtures of the tolyl acetates and nitrophenyl acetates to the appropriate conversion procedures, that there was no preferential loss of any isomer.

General Procedure.—Lead tetra-acetate was the B.D.H. laboratory reagent, which was moist with acetic acid. Immediately before use, the reagent was filtered under suction and stored in a vacuum-desiccator over potassium hydroxide pellets for 6 hr. The resulting white crystalline material was then usually about 95% pure as estimated by iodide titration.[41] When reactions were carried out in a solvent other than acetic acid, the lead tetra-acetate obtained as above was washed repeatedly with the appropriate solvent and, after filtration, was dried in a vacuum-desiccator; in these cases, a brownish material was obtained.

For reactions in acetic acid, lead tetra-acetate (2 g.) was added to a solution of the aromatic compound (0·2 ml.) in acetic acid (3 ml.). Experiments at the reflux temperature were carried out for 1 hr., those at 80° for 2 days, and those at 25° for 1 week. After reaction, the solutions were added to water and extracted several times with ether, and the ethereal extract was washed with aqueous sodium carbonate and dried. Reactions with anisole were also carried out in benzene and in anisole. Products from the reactions of benzene and toluene were determined by using column 1.

A solution of bibenzyl (1·6 g.) and lead tetra-acetate (4·4 g.) in acetic acid (10 ml.) was refluxed for 2 hr. Gas chromatography (column 5) gave two partially resolved peaks corresponding to products. After a solution of bibenzyl (0·11 g.), benzene (0·7 ml.), and lead tetra-acetate (4·4 g.) in acetic acid (10 ml.) had been refluxed for 1 hr., analysis (column 5), biphenyl being used as an external standard, showed that about 85% of the bibenzyl had been consumed, of which the two peaks corresponding to the products from bibenzyl accounted for about 20%.

The quantities of reactants and solvents stated above were used to measure the extents of acetoxylation of anisole in acetic acid and in benzene. Each solution was heated at 80° for 2 days, and the peak area on the gas chromatogram corresponding to *p*-acetoxyanisole was then

[39] Brooks, *Chem. and Ind.*, 1959, 1317.
[40] Norman, *Proc. Chem. Soc.*, 1958, 151.
[41] Dimroth and Schweizer, *Chem. Ber.*, 1923, **56**, 1375.

determined relative to that of an internal standard.   Comparison of each of two sets of experiments then gave values of 16·6 and 13·0 for relative amounts of *p*-acetoxyanisole formed in acetic acid and benzene, respectively.

Isolation of p-*Methoxyphenyl-lead Triacetate.*—(*a*) *From benzene.*   Lead tetra-acetate (70 g., 1 mol.) and anisole (20 g., 1·2 mol.) were heated in benzene (200 ml.) at 80° for 10 days. Addition of light petroleum (b. p. 40—60°) to the filtrate gave a white precipitate (6·3 g.), which was recrystallised from benzene containing a few drops of acetic acid.   The resulting material (7% yield) was identical (infrared spectrum) with authentic *p*-methoxyphenyl-lead triacetate [15] (Found: C, 32·0; H, 3·8.   Calc. for $C_{13}H_{16}O_7Pb$: C, 31·8; H, 3·3%).

(*b*) *From acetic acid.*   Lead tetra-acetate (22 g., 1 mol.) and anisole (7·5 g., 1·4 mol.) were heated in acetic acid (200 ml.) at 80° for 4 days.   After removal of acetic acid by vacuum-distillation, water (100 ml.) was added to destroy the residual lead tetra-acetate, and the solution was extracted with benzene.   Addition of light petroleum (b. p. 40—60°) to the extract gave a brownish precipitate (5·7 g.) which, after recrystallisation as above, gave *p*-methoxy-phenyl-lead triacetate (24% yield) as white crystals.

Decomposition of Organo-lead Compounds.—*p*-Methoxyphenyl-lead triacetate (0·08 g.) was heated in each of the solvents benzene, anisole, and acetic acid (2 ml.) at 80° for 2 days. *p*-Acetoxyanisole was not detected in any experiment, but small quantities of anisole and *p*-methoxybiphenyl were formed in acetic acid and in benzene, respectively.   The reactions were repeated in the presence of lead tetra-acetate (1 g.), but again no *p*-acetoxyanisole was detected.

Phenyl-lead triacetate (0·05 g.) was heated in anisole (2 ml.) at 80° for 2 days.   The identification of each of the methoxybiphenyls and measurement of their relative proportions were carried out by direct gas chromatographic analysis of this mixture.

Electrolytic Acetoxylation.—The cathode was a platinum disc (3 cm. in diameter), and the anode was a small square of platinum placed in a separate compartment provided with a porous sintered-glass diaphragm.   The electrodes were immersed in a solution of acetic acid (25 ml.) saturated with potassium acetate, the beaker which contained this solution being immersed in an ice-bath.   The aromatic compound (1 ml.) was placed in the anode compartment.   Electrolysis was carried out for 6 hr. with a constant current of 0·1 amp. and with rapid stirring of the solution.

The resulting solutions were added to water, and the ethereal extracts were washed with sodium carbonate and dried.   The acetoxyanisoles were analysed as such (column 2), the tolyl acetates were analysed as cresols (column 4), and the possible formation of nitrophenyl acetates was tested by submitting the solution to the hydrolysis and methylation procedures described above, but no nitroanisoles were detected.