Reactions of Lead (IV). Part XXIV.[1] Reactions with Some Benzenoid Compounds in the Presence of Monomethyl Oxalate

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Benzene undergoes methoxycarbonylation and methylation, and anisole these reactions as well as acetoxylation and oxidative dimerisation, when treated with lead tetra-acetate in the presence of monomethyl oxalate. Evidence is adduced that radical-chain reactions are involved in the formation of each type of product, that the methoxycarbonyl radical mediates in methoxycarbonylation, and that oxidative dimerisation occurs by electrophilic plumbylation followed by radical-chain processes.

WE have previously shown that benzenoid compounds can undergo two types of electrophilic reaction when treated with lead(IV). One is plumbylation, which has the characteristics of the S_E2 process;[2-5] the derived aryl-lead compound can undergo both homolytic and heterolytic fragmentations.[3-5] The second is an electron-transfer reaction which is electrophilic in the sense that it leads to an electron-deficient aromatic species, thought to be a radical cation;[1,4-6] this species can react with a nucleophile to give a cyclohexadienyl radical which can be further oxidised, and the entire process is of radical-chain type and can be initiated by Perkadox.[1,6]

We have now studied the reactions of anisole and benzene with lead tetra-acetate in the presence of monomethyl oxalate, and have found that the oxalate facilitates reactions of both types; the reactions which occur include homolytic substitution by the methoxycarbonyl radical.

RESULTS AND DISCUSSION

Monomethyl oxalate was obtained as a low-melting solid which, even after three fractionations, contained 0·5—1% of the dimethyl ester (g.l.c.) and possibly a trace of the acid. However, these were of no consequence for our studies since oxalic acid is rapidly decomposed to carbon dioxide by lead tetra-acetate and dimethyl oxalate did not react under our conditions; in control experiments it was found that monomethyl oxalate, when heated with lead tetra-acetate alone or in acetic acid, gives methyl acetate and dimethyl oxalate.

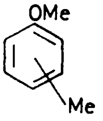
Reactions of aromatic compounds with lead tetra-acetate in the presence of monomethyl oxalate were continued until no lead tetracarboxylate remained, as judged by the lack of a precipitate of lead dioxide when a drop of the reaction mixture was added to water. G.l.c. was used for the quantitative analysis of the resulting products.

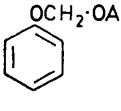
The reactions of anisole were studied with varying ratios of oxidant to monomethyl oxalate, both in air and under nitrogen, and, for the latter conditions, in the presence of a small quantity of Perkadox (di-isopropyl peroxydicarbonate). The major products are in the Table; yields are based on lead(IV). In addition, *o*- and *p*-chloroanisole were formed in up to 2% yield (*o* : *p*, *ca.* 1 : 6), as in other reactions of this type,[4,6] and are not considered further; in the two reactions in which Perkadox was included, the two isopropyl methoxyphenyl carbonates which have been found previously[1,6] were detected; and in experiment 6 there were traces of the phenoxymethylanisoles. Methyl acetate was never formed in more than 0·5% yield. The isomer distributions for ring-substituted products could only be measured with reasonable accuracy when yields were at least 1% and, for the products (3), only in experiment 3.

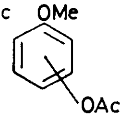
Products from the oxidation of anisole (10 ml) with lead tetra-acetate (1 g) in the presence of monomethyl oxalate at 80° (* with added Perkadox)

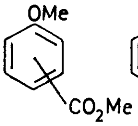
	$MeO_2C{\cdot}CO_2H$		Products (%)				
Expt.	(g)	Atmos.	(1)	(2)	(3)	(4)	(5)
1	0·5	Air	1 [a]	0·4	0·4	3 [c]	0·3
2	0·5	N_2	7 [a]	2	1	18 [c]	0·3
3 *	0·5	N_2	26 [a]	12	7 [b]	31 [c]	11 [d]
4	1	Air	1 [a]	0·7	0·5	10 [c]	3 [d]
5	1	N_2	5 [a]	2	1	20 [c]	0·5
6 *	1	N_2	14 [a]	6	3	46 [c]	13 [d]

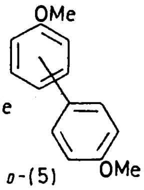
o : *m* : *p* Ratios: (*a*), 76 : 18 : 6; (*b*), 30 : 0 : 70; (*c*), 65 : 20 : 15; (*d*), 65 : 19 : 16.


o-(1)
m-(1)
p-(1)


(2)


o-(3)
p-(3)


o-(4)
m-(4)
p-(4)


o-(5)
m-(5)
p-(5)

The oxidation of benzene was studied under the conditions of experiments 2 and 3. In the former case, reaction was not complete even after 1 h, the products then being toluene (8%) and methyl benzoate (5%); even after 17 h, when reaction was complete, the yields were only 10 and 8%, respectively. However, reaction was complete within 1 h in the latter case (inclusion of Perkadox), the yields of toluene and methyl benzoate

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[1] Part XXIII, R. A. McClelland, R. O. C. Norman, and C. B. Thomas, preceding paper.

[2] F. R. Preuss and I. Janshen, *Arch. Pharm.*, 1960, **293**, 933.

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

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

[5] R. O. C. Norman, C. B. Thomas, and J. S. Willson, *J. Chem. Soc.* (*B*), 1971, 518.

[6] R. A. McClelland, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 1972, 562.

being 22 and 15%, with traces (<1%) of biphenyl, diphenylmethane, bibenzyl, benzyl acetate, and dimethyl phthalate.

We shall consider first the likely sources of each product and then the mechanisms of reaction.

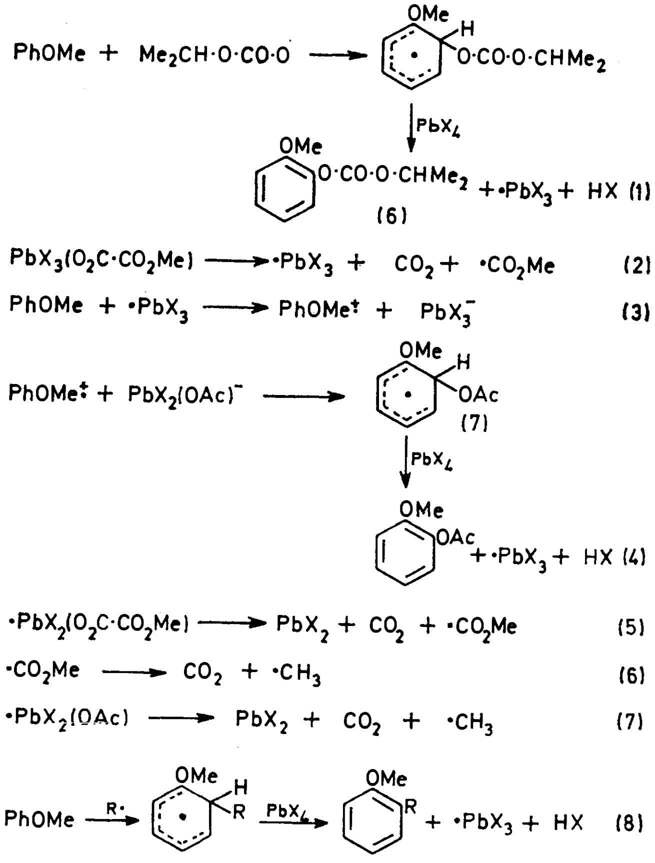
(a) *The methyl derivatives*. The isomer distribution for the methylanisoles is, within the limits of the experimental error, the same as in the absence of monomethyl oxalate ($o:m:p = 74:19:7$),[6] from which we infer that, as in that case, the methyl radical is the active entity. Now, there are three possible sources of this radical: Perkadox (by way of $Me_2CH{\cdot}O{\cdot}CO{\cdot}O \longrightarrow Me_2CH{\cdot}O{\cdot} \longrightarrow Me{\cdot}$), acetate groups, and monomethyl oxalate. A distinction between these was provided by our finding that, when lead tetra-acetate was replaced by the tetrapropionate for reaction under the conditions of experiment 6, methylation predominated over ethylation (mol ratio of methyl- to ethyl-anisoles, 91 : 9), whereas when monomethyl oxalate was replaced by monoethyl oxalate, ethylation predominated (mol ratio of methyl- to ethyl-anisoles, 10 : 90); moreover, in the latter case, the ratio did not fall when Perkadox was omitted. It follows that, in the lead tetra-acetate-monomethyl oxalate system, the oxalate is the major source of the methyl radical and the acetate is a minor source.

(b) *The methoxycarbonyl derivatives*. The relatively unselective isomer distribution in the reaction with anisole, and the predominance of *ortho*-substitution, suggest that methoxycarbonylation occurs by way of the radical $\cdot CO_2Me$. In order to be able to distinguish more clearly between reagents of electrophilic, nucleophilic, and radical type, we submitted mixtures of anisole and nitrobenzene to reactions under conditions corresponding to experiment 6. The methyl nitrobenzoates were formed at *ca.* 4 times the rate of the methyl methoxybenzoates, as judged by their relative yields, and their isomer distribution was $o:m:p = 66:3:31$. Thus, nitrobenzene, like anisole, is mainly *ortho*-orienting, eliminating the possibility of electrophilic or nucleophilic substitution but consistent with homolytic substitution. The relative reactivity of nitrobenzene and anisole is somewhat greater than in phenylation at the same temperature,[1] suggesting that the methoxycarbonyl radical, like the amido-radical,[7] has nucleophilic character.

(c) *The acetoxy-derivatives*. As in the reaction in the absence of the oxalate,[6] anisole gives ring-acetoxylated products whereas no phenyl acetate could be detected from benzene. We infer that reaction occurs by a similar mechanism, namely the electron-transfer process involving the anisole radical cation, benzene being markedly less reactive than anisole in this respect. The side-chain acetoxy-derivative (2) may also arise in the ways described before.[6]

(d) *The dimethoxybiphenyls*. Only the 2,4′-, 3,4′-, and 4,4′-isomers were detected, in contrast to the situation when these products result from the electron-transfer reaction.[5] The isomer distribution, within the experimental error, is the same as that for reaction of the *p*-methoxyphenyl radical with anisole ($o:m:p = 63:18:19$),[8] pointing to the mediation of the *p*-methoxyphenyl radical under our conditions.

Mechanisms of Reaction.—The yields of all the products from anisole are greater when reaction is under nitrogen compared with in air, and are further increased by the inclusion of Perkadox. These are characteristics of the reaction in the absence of the oxalate [6] and point to the operation of a radical-chain mechanism. For all products, except the dimethoxybiphenyls, the results for anisole are satisfactorily accommodated by the radical-chain mechanisms in the Scheme ($X = OAc$ or $OCO{\cdot}CO_2Me$ here and subsequently; only *ortho*-substituted intermediates and products are shown for simplicity). One method of initiation of the chains, when Perkadox is present, is likely to be *via* reaction (1), as evidenced by the detection of the carbonate (6) and its *para*-isomer, but since in the absence of Perkadox reaction is considerably faster than when the oxalate is omitted,[6] alternative modes of initiation are possible; one such may be reaction (2), and another is electron-transfer from anisole to lead(IV). However,



SCHEME

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[7] F. Minisci, G. P. Gardini, R. Galli, and F. Bertini, *Tetrahedron Letters*, 1970, 15.

[8] R. A. Abramovitch and O. A. Koleoso, *J. Chem. Soc.* (*B*), 1969, 779.

we infer that the first method is the most effective since, with anisole, yields are higher in experiments 3 and 6 than 2 and 5, respectively, and, with benzene, the rate of consumption of lead tetracarboxylates is greater when Perkadox is present. Reactions (3) and (4) constitute the chain-propagating steps for nuclear acetoxylation (*cf.* ref. 6). The methoxycarbonyl radical can be formed by reaction (5) and the methyl radical mainly by reaction (6) and to some extent by reaction (7) and possibly also by fragmentation of the adduct (7) and its *para*-isomer;[1,6] reactions (5), (6), and (7) together with reaction (8; R = Me• or •CO_2Me) constitute the propagating steps for methoxycarbonylation and methylation both for anisole and for benzene [PhH for PhOMe in reaction (8)].

There remains the mechanism of formation of the *p*-methoxyphenyl radical and thence the dimethoxybiphenyls. One established route to this radical which involves a lead(IV) intermediate is the Perkadox-induced decomposition of *p*-methoxyphenyl-lead triacetate.[4] Now, although plumbylation does not occur to a significant extent within the time of the experiments in the Table when anisole is treated with lead tetra-acetate, it is fairly rapid in the presence of acids which are much stronger than acetic acid (occurring, it appears, almost exclusively at the *para*-position).[5] Monomethyl oxalate is such an acid, so that it is reasonable to expect the formation of a derivative of the type *p*-$MeO{\cdot}C_6H_4{\cdot}PbX_3$ under the conditions of the experiments in the Table, followed by its homolysis to the *p*-methoxyphenyl radical.

To investigate this possibility, we first studied the decomposition of *p*-methoxyphenyl-lead triacetate in anisole in the presence of Perkadox for 12 h at 80° under nitrogen; the dimethoxybiphenyls were formed in 18% yield (isomer distribution the same as in the Table), together with small amounts (1—2%) of products (1)—(3). We then carried out experiment (1) again until no lead tetracarboxylate remained (10 min); at this point, a sample liberated iodine from potassium iodide, showing that some lead(IV) was still present, but in a form, such as an aryl-lead tricarboxylate, which does not form lead dioxide with water. [A control experiment showed that *p*-methoxyphenyl-lead triacetate in anisole liberates iodine from potassium iodide. However, iodometry could not be employed for the quantitative analysis of the lead(IV) since anisole reacts with iodine under these conditions.] When the solution was heated under nitrogen with Perkadox for a further 12 h, the dimethoxybiphenyls were formed in 16% yield (isomer distribution the same as in the Table) and small additional quantities of products (1)—(3) were obtained. We infer that, under the conditions of experiment 1, some *p*-methoxyphenyl-lead tricarboxylate is formed within 10 min, accounting in part for the low material balance recorded in the Table at that time, and that this can undergo homolysis to give the *p*-methoxyphenyl radical (and so the dimethoxybiphenyls) and a lead(III) derivative which can effect further formation of products (1)—(3). The rate of release of the *p*-methoxyphenyl radical from the aryl-lead compound is small as judged by the very low yield of the biaryls after 10 min in experiment 1, but can be greatly speeded by the inclusion of Perkadox, as shown by comparison of the results of experiments 2 and 5 with those of 3 and 6, respectively; we conclude that the aryl-lead compound, by accepting an electron from a substituted cyclohexadienyl radical, gives a *p*-methoxyphenyl radical and lead(II) and that the former, by reacting with anisole, gives cyclohexadienyl radicals which continue the chain.

EXPERIMENTAL

General methods w the as described in Part XXII.[6]

Materials.—Monomethyl oxalate was prepared by slowly distilling a stirred mixture of oxalic acid (100 g), methanol (150 ml), and carbon tetrachloride (600 ml) through a 50 cm column until the volume had been reduced to *ca.* 200 ml and then removing remaining volatile material on a rotary evaporator to leave a mixture of oxalic acid and its mono- and di-methyl esters. This mixture was distilled under reduced pressure through a 15 cm Vigreux column to give, first, dimethyl oxalate, m.p. 54—55° (lit.,[9] 54°), and then monomethyl oxalate which was twice redistilled to give material of b.p. 50—52° at 0·2 mmHg (lit.,[10] 108—109° at 12 mmHg). The material crystallised on cooling to give a white solid with a m.p. close to room temperature, but recrystallisation was unsuccessful. G.l.c. analysis showed that dimethyl oxalate (0·5—1%) was present; on standing, the proportion of this material rose and the sample liquefied, indicative of disproportionation with oxalic acid as the other product.

A similar procedure with ethanol in place of methanol gave monoethyl oxalate as a colourless liquid, b.p. 48° at 0·1 mmHg (lit.,[11] 88° at 4 mmHg).

p-Methoxyphenyl-lead triacetate was prepared as described previously.[3] Methoxy- and nitro-benzoate esters were prepared by esterification of the acids, and all other materials were commercially available or have been described previously.[6]

Oxidations.—Reactions were carried out by adding the lead(IV) salt to a stirred solution of the other reactants at 80° which, when required, had been deaerated and was under nitrogen. Work-up and analysis procedures were as before.[6] (In experiments 4 and 6, a sample was removed before work-up and analysed for methyl acetate.) Analysis of *p*-methoxyphenyl acetate was difficult because its g.l.c. peak overlapped with those of methyl *o*- and *m*-methoxybenzoate; a reliable value for the isomer distribution in acetoxylation could be obtained only in experiment 3. The results of experiments which are not detailed in the Discussion were as follows (all at 80° for 15 min unless stated otherwise).

(i) Lead tetrapropionate (1 g), monomethyl oxalate (1 g), Perkadox (*ca.* 50 mg), and anisole (10 ml), under nitrogen, gave methylanisoles (3·9%), ethylanisoles (0·4%), chloroanisoles (0·4%), phenoxymethyl propionate (3%), and methyl methoxybenzoates (30%, $o:m:p = 62:20:18$).

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

[10] Beilstein's Handbuch, Band 2, I, 534.

[11] C. Contzen-Crowet, *Bull. Soc. chim. belges*, 1926, **35**, 165.

Dimethoxybiphenyls and methoxyphenyl propionates were not analysed.

(ii) Monoethyl oxalate (1 g), lead tetra-acetate (1 g), Perkadox (0 and *ca.* 50 mg), and anisole (10 ml), under nitrogen, gave methylanisoles (1·6 and 1·5%), ethylanisoles (11 and 14%), chloroanisoles (2·1 and 2·1%), phenoxymethyl acetate (1·5 and 2%), methoxyphenyl acetates (1 and 2%), ethyl methoxybenzoates (11%, $o:m:p = 65:22:13$, and 12%, $o:m:p = 63:22:15$), and dimethoxybiphenyls (2 and 21%).

(iii) Mixtures of anisole and nitrobenzene (10 ml, 0·83 : 1 and 3·29 : 1, w/w), monomethyl oxalate (1 g), lead tetra-acetate (1 g), and Perkadox (*ca.* 50 mg), under nitrogen, gave methyl methoxybenzoates (0·9%, $o:m:p = 68:17:15$, and 2·9%, $o:m:p = 66:19:15$) and methyl nitrobenzoates (3·4%, $o:m:p = 66:3:31$, and 3·7%, $o:m:p = 65:3:32$). Other products, including methoxytoluenes and nitrotoluenes, were also present in small yields.

(iv) *p*-Methoxyphenyl-lead triacetate (0·8 g), Perkadox (50 mg), and anisole (10 ml), under nitrogen for 12 h, gave methylanisoles (2%), phenoxymethyl acetate (1%), methoxyphenyl acetates (1%), and dimethoxybiphenyls (16%, $2,4' : 3,4' : 4,4' = 68:16:16$).

(v) Part of the reaction mixture from experiment 1, upon completion, was deaerated and stirred under nitrogen at 80° for 12 h with Perkadox (*ca.* 50 mg). Products were methylanisoles (4%), phenoxymethyl acetate (2%), methoxyphenyl acetates (1%), methyl methoxybenzoates (10%, $o:m:p = 65:21:14$), d dimethoxybiphenyls (16%, $o:m:p = 65:17:16$).

(vi) Lead tetra-acetate (1 g) reacted with monomethyl oxalate (3 g) within 30 min at 80° and with monomethyl oxalate (1 g) in acetic acid (10 ml) within 4 h at 80°. A sample was removed for analysis of methyl acetate (Carbowax, 80°) and the remainder was washed quickly with sodium hydrogen carbonate solution and analysed for other products, only dimethyl oxalate being detected [acid-washed DEGA (10%) coated on Celite]; control experiments showed that our method of work-up would have removed only *ca.* 10% of the dimethyl oxalate present. The yields of products, in the absence and presence, respectively, of acetic acid, were: methyl acetate, 23 and 62%; dimethyl oxalate, 55 and 18%. When lead diacetate (0·7 g) was used in place of the tetra-acetate, reactions as above and for the same times gave methyl acetate (5 and 6%, respectively) and dimethyl oxalate (14 and 4%, respectively) [yields based on lead(II)]. When no lead salt was present, only traces of the products were formed.

In control experiments, portions (50 ml) of a solution of potassium iodide (9·6 g), sodium carbonate (50 g), and sodium acetate (45 g) in water (1 l) were added to (i) a sample of the reaction mixture from experiment 1, in acetic acid, and (ii) *p*-methoxyphenyl-lead triacetate, in anisole and acetic acid. Iodine was liberated in each case.

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