

Reactions of Lead(IV). Part XXIII.¹ Reactions of Lead Tetrabenzoate with Some Benzenoid Compounds, and Comparison with Those of Dibenzoyl Peroxide

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Lead tetrabenzoate effects, principally, the phenylation and benzoyloxylation of anisole by radical-chain processes which can give nearly quantitative yields; in contrast, benzene and nitrobenzene undergo only phenylation. It is argued that the anisole radical cation mediates in benzoyloxylation, and other characteristics of the chain reactions are discussed. Differences between lead tetrabenzoate and dibenzoyl peroxide as oxidants for benzenoid compounds have been explored; the chief differences are the much smaller capacity of the latter to oxidise by one-electron acceptance, and the fact that benzoyloxylation of anisole by the peroxide does not occur *via* formation of the anisole radical cation. Nonetheless, there is evidence that this radical cation can be formed from the adducts of the benzoyloxy-radical with anisole, and that this is an acid-catalysed reaction which competes with oxidation of the adducts to the benzoyloxyanisoles.

WE have shown in the preceding paper that anisole reacts with lead tetra-acetate in a radical-chain process initiated by Perkadox (di-isopropyl peroxydicarbonate).¹ Key features of the process for which evidence was adduced are as follows: a lead(III) species abstracts

one electron from anisole to give the aromatic radical cation which, with acetate ion, yields substituted cyclohexadienyl radicals; these, with lead(IV), give

¹ Part XXII, R. A. McClelland, R. O. C. Norman, and C. B. Thomas, preceding paper.

acetoxyated products and lead(III) which continues the chain. The lead(III) species also fragments to the methyl radical, and this effects methylation of anisole *via* cyclohexadienyl radicals, oxidation of which again leads to replacement of lead(III). Finally, the chain involved in methylation is diverted by bromotrichloromethane but that involved in acetoxylation is not.

We now report on similar studies with lead tetrabenzoate as the oxidant. One of the features of interest attaching to this compound is that, whereas the acetoxy-radical, which in principle can be formed from lead tetra-acetate, could only act as a source of the methyl radical because of its exceptionally rapid homolysis to give that species, the benzyloxy-radical, which in principle can be derived from the tetrabenzoate, is much more resistant to homolysis and might therefore play a significant role in the reaction scheme. Our

phenyl [82%, which was reduced to 53% when benzoic acid was included] but no phenyl benzoate (0.05% of which would have been detected by the g.l.c. method). When a large excess of a mixture of anisole and benzene was oxidised, the product distribution showed anisole to be 1.6 times as reactive as benzene in phenylation and at least 1000 times as reactive in benzyloxylation (phenyl benzoate again being undetectable). The oxidation of nitrobenzene, under the same conditions as benzene, required longer (2 h) and gave the nitro-biphenyls (41 and 46%, respectively, with and without benzoic acid); the distribution of the *ortho*-, *meta*-, and *para*-isomers was 45:18:37% in each case. The yields of phenylation products in a competitive reaction between nitrobenzene and benzene showed the former to be more reactive in this process by a factor of 2.2.

When bromotrichloromethane was included for the

TABLE 1

Products from the oxidation of anisole with lead tetrabenzoate in the presence of Perkadox under nitrogen at 80° for 10 min

Expt.	Pb(OBz) ₄ (g)	PhOMe (ml)	PhCO ₂ H (g)	Products (%)				Ratio (<i>o</i> -4) : (<i>p</i> -4)	Total Pb ^{IV} accounted for (%)
				(1)	(2)	(3)	(4)		
1	1	100	0	39 ^b	12	2	37	25 : 75	90
2	1	10	0	16 ^b	6.5	0.5	73	31 : 69	96
3	1.2	9	1	6 ^b	6	—	86	27 : 73	98
4	1.4	10	5	7 ^b	10	—	76	24 : 76	93
5	0.5	50	25	6	1	0.1	30	22 : 78	37
6 ^a	0.6	50	25	12 ^b	2	—	45	22 : 78	59

^a Cu(OBz)₂ (86 mg) was included. ^b *o* : *m* : *p* = 65 : 20 : 15.

TABLE 2

Products from the oxidation of anisole under the conditions of the experiments in Table 1, in the presence of bromotrichloromethane

Expt.	Pb(OBz) ₄ (g)	PhOMe (ml)	BrCCl ₃ (ml)	Products (%)			PhBr ^a	MeO-C ₆ H ₄ -Br
				(2)	(4)	Ratio (<i>o</i> -4) : (<i>p</i> -4)		
7	0.7	10	1	12	60	41 : 59	20	9 ^b
8	0.5	1	5	9	48	45 : 55	30	37 ^b

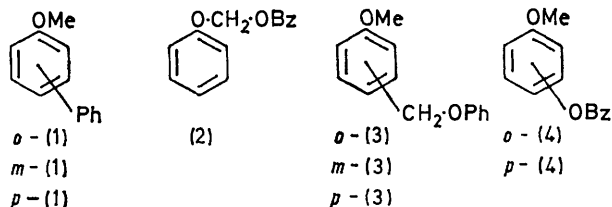
^a See text. ^b *o* : *m* : *p* = 2 : 0 : 98.

wish to investigate this possibility led us also to examine the behaviour of dibenzoyl peroxide under comparable conditions, since this is an established source of the benzyloxy-radical.

Reactions of Lead Tetrabenzoate.—Lead tetrabenzoate was prepared from the tetra-acetate and benzoic acid² and shown by iodometry to contain 90% lead(IV); allowance was made for this in the yields quoted, which are based on lead(IV) and the assumption that 1 mol of each product requires 1 mol of lead(IV). Reactions were carried out in the presence of *ca.* 50 mg of Perkadox, at 80° under nitrogen.

The products from anisole are in Table 1; in addition, small quantities of isopropyl *o*- and *p*-methoxyphenyl carbonate were detected. Reactions were complete within 10 min, and neither *m*-benzyloxyanisole nor any of the dimethoxybiphenyls were detectable. Benzene, under similar conditions (0.5 g of oxidant in 10 ml of benzene), was oxidised within 20 min and gave bi-

oxidation of anisole, neither the methoxybiphenyls (1) nor the phenoxymethylanisoles (3) could be detected; the products are in Table 2. (Bromobenzene could be detected but not estimated because of interference



of its g.l.c. peak with that from anisole; the yields in Table 2 refer to those obtained in exactly analogous reactions with phenetole in place of anisole.) With benzene, the yield of biphenyl was reduced to 0.4%,

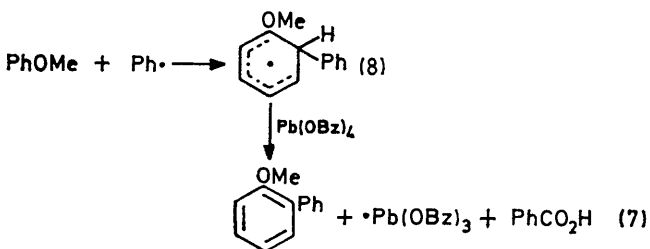
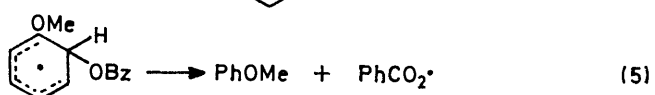
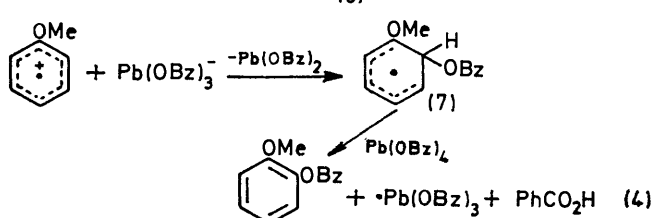
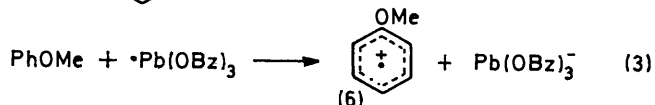
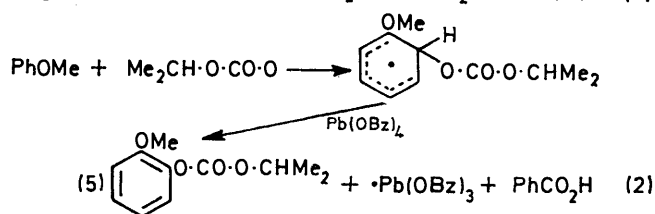
² D. H. Hey, C. J. M. Stirling, and G. H. Williams, *J. Chem. Soc.*, 1954, 2747.

bromobenzene (78%) and benzotrichloride (85%) being the principal products. With nitrobenzene, the yield of nitrobiphenyls was reduced to 3% and the major product detected was bromobenzene (68%) (in neither this case nor with anisole would the analytical technique necessarily have revealed the presence of trichloromethylated derivatives).

The results show close analogies to those obtained with lead tetra-acetate in the presence of Perkadox, and in particular we note the following. First, reaction is considerably faster than in the absence of Perkadox (when, for example, 15 h is required for reaction in nitrobenzene² at 125°), implying that a radical-chain process is involved; moreover, the aryl isopropyl carbonates (5) and its *para*-isomer are formed, consistent with initiation of the chain by reactions (1) and (2). Secondly, anisole gives nuclear and side-chain benzyloxylation products, and it, benzene, and nitrobenzene undergo phenylation. The isomer distribution in the phenylation of anisole and nitrobenzene, and the reactivities of these compounds relative to that of benzene, are *similar* to those reported for other sources of the phenyl radical at 80°; we assume that the phenyl radical is responsible in this case and discuss the data more fully later. The far higher reactivity of anisole than benzene in benzyloxylation, in contrast, is inconsistent with reaction by way of addition of the benzyloxy-radical to the aromatic ring followed by oxidation (*cf.* refs. 3, 4, and later discussion) and points to the electron-transfer process implicated in acetoxylation¹ [indeed, as we show later, the benzyloxy-radical is probably not formed directly from lead tetrabenzoate or $\cdot\text{Pb}(\text{OBz})_3$ in this system]. The material balance is high, although it falls as the concentration of the oxidant is reduced; however, in general the ratio of the amounts of benzyloxylation to phenylated products is much greater than that of the amounts of acetoxylation to methylated products with lead tetra-acetate. Thirdly, bromotrichloromethane does not inhibit the radical-chain reaction which gives the benzyloxy-derivatives of anisole but does inhibit phenylation. We therefore infer that the mechanisms of reaction are essentially the same with lead tetrabenzoate as with the tetra-acetate, as shown in Scheme 1 for the oxidation of anisole (for simplicity, only *ortho*-substituted species are represented); the paths for the oxidation of benzene and nitrobenzene are analogous except for the lack of occurrence of the steps corresponding to reactions (3)–(5), and we make the following comments.

(a) Lead tetrabenzoate is more efficient than the tetra-acetate at effecting acyloxylation; thus, the latter oxidant, under conditions closely similar to those of experiments 1 and 3, gave only 2 and 21% acetoxylation, respectively (the major products being methyl-anisoles, 70 and 36%, respectively). We attribute this to the somewhat greater electron affinity of a benzyloxy-compared with an acetoxy-group; the species $\cdot\text{Pb}(\text{OBz})_3$ should be a more effective oxidant for anisole [reaction (3)] than $\cdot\text{Pb}(\text{OAc})_3$, its fragmentation [reaction (6)]

playing a correspondingly smaller part, and the adduct (7) and its *para*-isomer should be more efficiently oxidised by lead tetrabenzoate than the corresponding acetoxy-adducts by the tetra-acetate, rendering reaction (5)



SCHEME 1

(and thence another route to the phenyl radical) less probable than the corresponding reaction in the acetate series.

(b) The much longer time required for consumption of the oxidant with nitrobenzene as compared with benzene or anisole can be ascribed to the electron-attracting capacity of the nitro-group; thus, the one-electron oxidation of a cyclohexadienyl radical presumably gives a cyclohexadienyl cation in passage to the product and so should be slower for the adduct (8; NO₂ for OMe) than for (8) or (8; H for OMe), so that the chains are shorter for nitrobenzene than for the other two compounds.

(c) We considered the possibility that the species $\cdot\text{Pb}(\text{OBz})_3$ gives the benzyloxy-radical as an inter-

³ M. E. Kurz and M. Pellegrini, *J. Org. Chem.*, 1970, **35**, 990.

⁴ T. Nakata, K. Tokumaru, and O. Simamura, *Tetrahedron Letters*, 1967, 3303.

mediate in the formation of the phenyl radical, and rejected it, at least as a significant alternative to reaction (6), on the following grounds. The thermal and photochemical reactions of dibenzoyl peroxide with benzene under nitrogen give small but significant amounts of phenyl benzoate;^{4,5} as increasing pressures of oxygen are employed in the photochemical reaction, the yield of this product rises sharply.⁴ The inference, supported by other evidence,⁶ is that the benzoyloxy-radical adds reversibly to benzene and the adduct is only efficiently converted into phenyl benzoate when an oxidant is included.^{4,6} We found that the reaction of *ca.* 2 mmol of dibenzoyl peroxide in 40 ml benzene at 80° under nitrogen for 60 h gave only 2.7% phenyl benzoate, whereas, when 1 mmol of lead tetra-acetate was included, 4% was formed in 1 h, suggesting that lead(IV) can oxidise the intermediate cyclohexadienyl radical. Moreover, the yield was increased to 7% (based on peroxide) or 20% (based on lead tetrabenzoate) when *ca.* 1 mmol of the latter was included instead of lead tetra-acetate. Thus, since lead tetrabenzoate, like the tetra-acetate, oxidises the adduct of the benzoyloxy-radical and benzene to phenyl benzoate, the absence of this product in the Perkadox-catalysed reaction of lead tetrabenzoate and benzene implies that the benzoyloxy-radical is not present in significant amount [*cf.* evidence that the species $\cdot\text{Pb}(\text{OCOR})_3$ (R = alkyl) fragment directly to alkyl radicals⁷]. However, in reactions with anisole, there is another possible route to the benzoyloxy-radical (and thence the phenyl radical), namely fragmentation of the adduct (7) and its *para*-isomer [reaction (5)]. This path should become increasingly important as the probability of one-electron oxidation of these adducts is reduced, and this may underlie the significant increase in the ratio of phenylated to benzoyloxy products when the concentration of lead tetrabenzoate is reduced (compare experiments 1 and 2).

(d) As with lead tetra-acetate, the radical species involved in formation of the benzoyloxy-derivatives are not scavenged by bromotrichloromethane, whereas the phenyl radical is essentially completely trapped. In the reaction with benzene, in which the phenyl radical is likewise effectively trapped by bromotrichloromethane, reaction is nevertheless still complete in approximately the same time as in the absence of the bromo-compound. Thus, bromotrichloromethane acts as a chain transfer agent; we infer that its reaction with the phenyl radical to give bromobenzene (78%) and the trichloromethyl radical is followed by efficient trapping of the latter radical by benzene, the resulting substituted cyclohexadienyl radical being efficiently oxidised by lead(IV) to give benzotrichloride (85%) and lead(III) which perpetuates the chain.

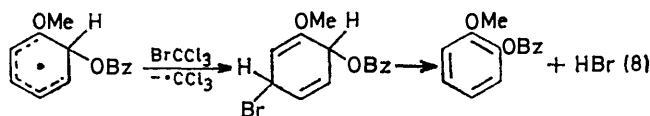
⁵ G. R. Chalfont, D. H. Hey, K. S. Y. Liang, and M. J. Perkins, *J. Chem. Soc. (B)*, 1971, 233.

⁶ J. Saltiel and H. C. Curtis, *J. Amer. Chem. Soc.*, 1971, **93**, 2056.

⁷ J. K. Kochi, J. D. Bacha, and T. W. Bethea III, *J. Amer. Chem. Soc.*, 1967, **89**, 6538.

(e) The phenoxy-methylanisoles (3) are presumably formed by reaction of anisole with the radical $\text{PhOCH}_2\cdot$; they have been observed previously as products from anisole and di-*t*-butyl peroxide.⁸ The phenoxy-methyl radical is likely also to be the source of the side-chain benzoyloxy-derivative (2), *via* its one-electron oxidation (this product is also formed from anisole with *t*-butyl perbenzoate⁹). It is notable that the product (2) is formed in the presence of bromotrichloromethane whereas the phenylated products are not; we infer that the reaction of anisole with the phenyl radical is not the only source of $\text{PhOCH}_2\cdot$ but that, as with lead tetra-acetate, the latter radical can also be formed from the radical cation (6) by loss of a proton. Since the phenoxy-methylanisoles (3) are not formed in the presence of bromotrichloromethane, we further conclude that, under these conditions, one route to the benzoyloxy-derivative (2) involves the sequence, (6) \rightarrow $\text{PhOCH}_2\cdot \rightarrow$ PhOCH_2Br (with CBrCl_3) \rightarrow $\text{PhO}\cdot\text{CH}_2\cdot\text{O}\cdot\text{COPh}$ (with benzoic acid).

Finally, the *ortho*:*para* ratio for the benzoyloxylation of anisole varies significantly with the conditions of the experiments in Table 1; factors similar to those responsible for the analogous variation in acetoxylation¹ may be responsible. It is notable that a more drastic change in this ratio occurs in the presence of bromotrichloromethane (Table 2). Possibly the radical (7) and its *para*-isomer are trapped by the bromo-compound to give cyclohexadienes which lose hydrogen bromide [*e.g.* reaction (8)], the selectivity between the radical (7) and its *para*-isomer in the trapping process being somewhat different from that in the one-electron oxidations [*e.g.* reaction (4)]; the hydrogen bromide could act to continue the chain by reducing lead(IV).



Reactions of Dibenzoyl Peroxide.—The products from the oxidation of anisole with dibenzoyl peroxide under nitrogen are in Table 3; yields are based on the peroxide, with the assumption that 1 mol of each product requires 1 mol of oxidant. The phenylated and nuclear benzoyloxy products have been identified previously in this reaction, and our isomer distributions are similar to those reported;^{10,11} in addition, we obtained the phenoxy-methylanisoles (3) (mainly the *ortho*-isomer, as with di-*t*-butyl peroxide⁸) and the side-chain benzoyloxy product (2). In a competitive reaction, with an excess of anisole and benzene relative to oxidant,

⁸ H. B. Henbest, J. A. W. Reid, and C. J. M. Stirling, *J. Chem. Soc.*, 1961, 5239.

⁹ S. Lawesson, C. Berglund, and S. Grönwall, *Acta Chem. Scand.*, 1961, **15**, 249.

¹⁰ B. M. Lynch and R. B. Moore, *Canad. J. Chem.*, 1962, **40**, 1461.

¹¹ R. T. Morrison, J. Cazes, N. Samkoff, and C. A. Howe, *J. Amer. Chem. Soc.*, 1962, **84**, 4152.

anisole was found to be more reactive than benzene in phenylation by a factor, $k_{rel.}$, of 2.2.

TABLE 3

Products from the oxidation of anisole with dibenzoyl peroxide (1 g) under nitrogen at 80° for 60 h

Expt.	PhOMe (ml)	PhCO ₂ H (g)	Products (%)			
			(1)	(2)	(3)	(4)
9	20	0	45 ^a	3	11	4 ^b
10	20	5	29 ^a	3	8	8 ^b

^a $o : m : p = 69 : 15 : 16$. ^b $o : p = 52 : 48$.

When the last experiment was repeated in the presence of copper(II) benzoate, the isomer distribution for phenylation changed to $o : m : p = 64 : 20 : 16$, and $k_{rel.}$ to 1.5. These values are, within the experimental error, the same as those obtained with lead tetrabenzoate, and this is consistent with the view that the cyclohexadienyl radical (8), its isomers, and the corresponding adduct from benzene, are efficiently oxidised to phenylated products by copper(II) or lead(IV) but not by dibenzoyl peroxide; with the last oxidant, alternative reactions for the intermediate radicals, such as dimerisation, are important, and occur with a different selectivity among the various radicals (*cf.* ref. 12). The data we have mentioned, and those for related reactions at 60°, are collected in Table 4 and demonstrate

TABLE 4

Isomer distributions for the phenylation of anisole and relative reactivity ($k_{rel.}$) of anisole and benzene

Source of Ph·	Temp.	Isomer ratio (%)			$k_{rel.}$	Ref.
		<i>o</i>	<i>m</i>	<i>p</i>		
(PhCOO) ₂	80°	70	14	16	2.0	11
(PhCOO) ₂	80	69	15	16	2.2	<i>a</i>
(PhCOO) ₂ -Cu ^{II}	80	64	20	16	1.5	<i>a</i>
Pb(OBz) ₄	80	65	20	15	1.6	<i>a</i>
PhN·NCPPh ₃	60	69	21	10	2.3	13
PhN ₂ ⁺ BF ₄ ⁻	60	59	17	24	1.9	14

^a This work.

TABLE 5

Isomer distributions for the phenylation of nitrobenzene and relative reactivity ($k_{rel.}$) of nitrobenzene and benzene

Source of Ph·	Temp.	Isomer ratio (%)			$k_{rel.}$	Ref.
		<i>o</i>	<i>m</i>	<i>p</i>		
(PhCOO) ₂	80°	58	10	32	2.94	15
(PhCOO) ₂	80	56	12	32	2.9 ^a	<i>b</i>
(PhCOO) ₂ -Cu ^{II}	80	57	12	31		<i>b</i>
Pb(OBz) ₄	80	45	18	37	2.2	<i>b</i>
PhN ₂ ⁺ BF ₄ ⁻	60	59	14	27	3.0	14
PhN·NCPPh ₃	60	79	7	14	4.4	13

^a Obtained from experiment 15 (Table 6), in the presence of acetic acid. ^b This work.

the ambiguities which can be associated with interpretation of the partial rate factors for homolytic aromatic substitution.

¹² D. H. Hey, K. S. Y. Liang, and M. J. Perkins, *Tetrahedron Letters*, 1967, 1477.

¹³ M. Kobayashi, H. Minato, N. Watanabe, and N. Kobori, *Bull. Chem. Soc. Japan*, 1970, **43**, 258.

The reaction of nitrobenzene with dibenzoyl peroxide, under the conditions used for anisole, gave 76% of nitrobiphenyls and *ca.* 1% biphenyl. The isomer distribution for the nitrobiphenyls, $o : m : p = 56 : 12 : 32$, remained essentially unchanged when copper(II) benzoate was included. This in itself could be understood given that nitrobenzene, and products derived therefrom, act as oxidants for cyclohexadienyl radicals,⁵ but in that case it is not clear why the distribution is different from that obtained with lead tetrabenzoate. We can offer no explanation, but note that, as some of the other data in Table 5 show, the quantitative results for the phenylation of nitrobenzene vary markedly with the conditions.

We examined the effect of Perkadox on the reactions of anisole with dibenzoyl peroxide by measuring the yields of products after reaction for only 1 h at 80° under nitrogen, first without and then with the inclusion of Perkadox; the yields under the former conditions for the products (1)–(4) were 23, 1.5, 2, and 2%, respectively, and each was increased by a factor of *ca.* 20% under the latter conditions [when traces of the carbonate (5) and its *para*-isomer were also detected]. This small effect is in marked contrast to the large influence which Perkadox plays in the reactions of anisole with lead tetrabenzoate and can be attributed to the fact, for which we have already presented evidence, that the peroxide is much less efficient than lead tetrabenzoate in oxidising cyclohexadienyl radicals; thus, the radical chains are much shorter with the peroxide.

When bromotrichloromethane was included in the oxidation of benzene by dibenzoyl peroxide, the yield of biphenyl was reduced from 45 to *ca.* 1%, that of phenyl benzoate was unchanged (*ca.* 2.5%), and bromobenzene (160%) and benzotrichloride (11%) were formed. Thus, the phenyl radical, but not the benzoyloxy-radical, is efficiently trapped. (The yield of bromobenzene in excess of 100% indicates that *both* phenyl groups in the peroxide can form phenyl radicals.) The results are again in marked contrast to those with lead tetrabenzoate, but as before can be accounted for in terms of the weaker one-electron oxidising capacity of the peroxide; thus, the adduct of benzene with the trichloromethyl radical is less efficiently oxidised by the peroxide than by lead tetrabenzoate (which gave benzotrichloride in 85% yield), so that most of the peroxide eventually yields phenyl radicals.

Finally, we turn to the question of whether the benzoyloxylation of anisole by dibenzoyl peroxide occurs by way of the radical cation (6) and thence the adduct (7) and its *para*-isomer or *via* addition of the benzoyloxy-radical to the aromatic ring to give these adducts directly (Scheme 2). We note, first, that anisole is far more reactive than benzene in benzoyloxylation with lead tetrabenzoate (a minimum value for the

¹⁴ R. A. Abramovitch and O. A. Koleoso, *J. Chem. Soc. (B)*, 1968, 1292.

¹⁵ D. H. Hey, S. Orman, and G. H. Williams, *J. Chem. Soc.*, 1961, 565.

relative reactivity is 1000), but only a few times more reactive when dibenzoyl peroxide is the reagent [we obtained the ratio 8 : 1, which is comparable with those (10 : 1 and *ca.* 4 : 1) reported for somewhat different conditions^{3,4}]. Therefore, if, as we believe, the radical cation (6) mediates in the reaction with lead tetra-benzoate, then the benzoyloxy-radical (or dibenzoyl peroxide) would have to be far less selective (*i.e.* more reactive) as a one-electron abstracting reagent than the lead species, which is *a priori* unlikely. We sought further information as follows.

If the species (6) mediates in the peroxide reaction, it should be capable of reacting not only with (a source of) benzoate ion, leading to benzoyloxy-derivatives, but also with other nucleophiles. When we carried out the reaction between anisole and dibenzoyl peroxide in the presence of acetic acid, we obtained, in addition to the products formed in the absence of the acid, the methylanisoles (9) (the isomer distribution amongst

In order to decide between these possibilities, we studied the oxidations of benzene and nitrobenzene with dibenzoyl peroxide in the presence of acetic acid. The yields of methylated products were negligible; the results of experiments 12 and 14 are essentially the same as in the absence of acetic acid, with high yields of phenylated products. However, when anisole was also present (experiments 13 and 15), the yields of phenylated products were drastically reduced and those of methylated products were significantly increased; the isomer distribution for the nitrotoluenes agrees closely with the literature value for reaction with the methyl radical at a higher temperature¹⁷ and we infer its mediation here. This marked effect of anisole on the reactions of benzene and nitrobenzene is in accord with the mediation of the radical cation (6) and thence the adduct (12) from which the methyl radical is derived by fragmentation, but not with the other two possibilities we have suggested.

TABLE 6

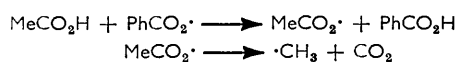
Oxidation of anisole, benzene, and nitrobenzene with dibenzoyl peroxide in the presence of acetic acid (1 ml) under nitrogen at 80° for 60 h

Expt.	PhOMe (ml)	PhX (ml)	Products (%)								X·C ₆ H ₄ Me	X·C ₆ H ₄ Ph
			(1)	(2)	(3)	(4)	(9)	(10)	(11)			
11	5	0	5 ^d	2	7	4 ^e	23 ^f	0.2	1			
12 ^a	0	5 ^b								1 ^b	62 ^b	
13 ^a	5	5 ^b	8 ^d	2	2	3 ^e	22 ^f	0.1	4	16 ^b	4 ^b	
14 ^a	0	5 ^c								<0.1 ^c	61 ^{e,h}	
15 ^a	5	5 ^c	4 ^d	0.2	0.2	11 ^e	1	0.1	1	12 ^{e,g}	6 ^{e,h}	

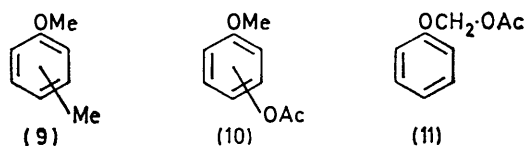
^a Phenyl benzoate (*ca.* 1%) was also detected. ^b X = H. ^c X = NO₂. ^d *o* : *m* : *p* ratios: ^d 68 : 13 : 19. ^e 57 : 0 : 43. ^f 78 : 18 : 4. ^g 63 : 7 : 30. ^h 58 : 11 : 31.

which indicated that the methyl radical was the active entity) and the acetoxyanisoles (10) and (11) (experiment 11, Table 6). This is consistent with the reaction of the radical cation (6) with acetic acid to give the adduct (12) and its *para*-isomer, oxidation of which leads to the nuclear acetoxyated anisoles and fragmentation of which gives the methyl radical and thence methylated products (the side-chain acetoxyated product is presumably formed from PhOCH₂· in the way described earlier). Further, when experiment 11 was carried out with the inclusion of copper(II) acetate, the yield of acetoxyanisoles increased to 8%, compatible with the increased importance of reaction (15) compared with reaction (14). Likewise, with propionic acid instead of acetic acid under the conditions of experiment 11, we obtained, *inter alia*, the ethylanisoles (19%; *o* : *m* : *p* = 77 : 20 : 3).

However, there are alternative paths which could account for the formation of the products (9)—(11) with acetic acid; thus, dibenzoyl peroxide and acetic acid might give the mixed peroxide, PhCO·O·O·COMe, and thence acetoxy- and, *somewhat*, benzoyloxy-radicals, or the benzoyloxy-radical might react with acetic acid to give those radicals (*cf.* ref. 16):



However, while we can now infer the intervention of the species (6) in the reaction of dibenzoyl peroxide and anisole, at least in the presence of acetic acid, it

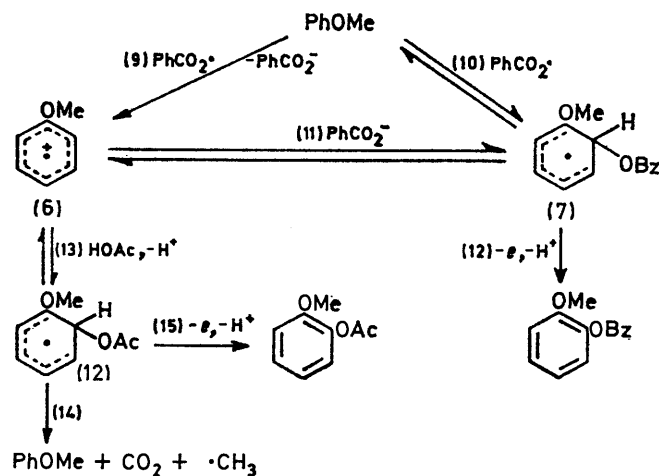


does not follow that benzoyloxylation occurs by the electron-transfer mechanism, that is, by reaction (9) followed by reactions (11) and (12); an alternative is that benzoyloxylation occurs by way of reactions (10) and (12) and that the species (6) is formed from the adduct (7) and its *para*-isomer by the reverse of reaction (11). To investigate this question further, we carried out the oxidation of anisole with dibenzoyl peroxide under the conditions previously employed by Kurz and Pellegrini,³ that is, with acetonitrile as a solvent [containing copper(II) chloride], so that we could examine the effect of the inclusion of acetate ion as opposed to acetic acid. The results are in Table 7 and include also a study of the effect of trifluoroacetic acid.

¹⁶ W. H. Starnes, jun., *J. Org. Chem.*, 1966, **31**, 1436.

¹⁷ B. R. Cowley, R. O. C. Norman, and W. A. Waters, *J. Chem. Soc.*, 1959, 1799.

The data show that, whereas the inclusion of acetic acid results in a marked reduction of the yield of the benzoyloxy-products (4) and the incursion of the acetoxy-derivatives (10) and (11), the inclusion of lithium acetate produces a far smaller change. [We



SCHEME 2

should not expect methylation to accompany acetoxylation since the methyl radical should be readily oxidised by copper(II) chloride.] We conclude that acetic acid acts mainly by providing protons, and that the data

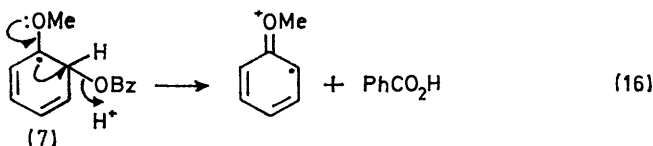
TABLE 7

Oxidation of anisole (5 ml) with dibenzoyl peroxide (0.5 g) in acetonitrile (30 ml) containing copper(II) chloride (0.1 g) under nitrogen at 80°

Expt.	Products (%)				
	(1)	(4)	(10)	(11)	Cl·C ₆ H ₄ ·OMe ⁱ
16	4.5	50 ^a			5
17 ^a	4.5	23 ^e	4 ^h	1	24
18 ^b	4	6 ^f			37
19 ^c	4	40 ^g	0.2	0.1	5.5

^a With HOAc (1 g). ^b With CF₃CO₂H (1 g). ^c With LiOAc (1 g). *o*:*p* ratios: (d), 65:35; (e), 70:30; (f), 74:26; (g), 66:34; (h), 61:39; (i), 4:96.

are not consistent with the occurrence of benzoyloxylation by way of the reaction sequence (9), (11), and (12) and of acetoxylation by the related sequence (9), (13), and (15), but are in accord with the occurrence, first, of reaction (10) and then of reaction (12) or, with acid



catalysis, the reverse of reaction (11), *i.e.* reaction (16).^{*} A further observation is notable in this context.

^{*} There is evidence for the acid-catalysed removal of the benzoate ion from adducts of toluene and phenylacetic acid with the benzoyloxy-radical¹⁸ and indications of the acid-catalysed removal of hydroxide ion from adducts of anisole with the hydroxy-radical.¹⁹

When reactions were carried out under the conditions of experiments 16–18 but without the inclusion of peroxide, the yields of the chloroanisoles were approximately the same as (with trifluoroacetic acid, fractionally greater than) in experiments 16 and 19. We infer, first, that in experiments 16 and 19 the chloroanisoles are formed by a route which is independent of the peroxide and, secondly, that in large part their formation in experiments 17 and 18 involves both peroxide and acid. The latter conclusion is in accord with the view that acid catalyses formation of the radical cation (6), from which the chloroanisoles can be formed by reaction with chloride ion followed by one-electron oxidation; further, that trifluoroacetic acid, compared with acetic acid, should more substantially increase the yield of the chloroanisoles, and decrease that of the benzoyloxy-derivatives, is consistent with its greater acid strength.

Two further aspects of the data in Table 7 deserve comment. First, the yield of the phenylisoles (1) is unchanged when that of the benzoyloxy-derivatives (4) is reduced in the presence of acid. We infer that the phenyl radical comes mainly from the benzoyloxy-radical directly and not by fragmentation of the adduct (7) and its *para*-isomer, and this in turn implies that the other paths available to these adducts—one-electron oxidation and acid-catalysed fragmentation—are very efficient under conditions of the experiments in Table 7. Secondly, the direction of the change in the *ortho*:*para* ratio of the benzoyloxy-derivatives (4) when acid is included suggests that the acid-catalysed fragmentation of the adduct (7) is somewhat less rapid than that of its *para*-isomer.

EXPERIMENTAL

General experimental details are as described in the preceding paper.¹ In addition, a g.l.c. column containing 10% Silicone MS550 coated on Celite was used for the analysis of high-boiling material.

Materials.—Lead tetrabenzoate was prepared essentially as described previously.² Lead tetra-acetate (12 g) and benzoic acid (16 g) were thoroughly mixed and heated under suction to 120–125°, at which point acetic acid is liberated from the molten mass. After 10–15 min, the residue was cooled, powdered, extracted with sodium-dried ether to remove excess of benzoic acid, and dried in a desiccator over phosphorus pentoxide. This sample had m.p. 188–191° [lit.,² 176° (dec.)]; its n.m.r. spectrum [in dry (P₂O₅) dichloromethane] showed it to be free of acetate [τ 1.87 (2H, m) and 2.44 (3H, m)]. Iodometric analysis (as in ref. 2) gave 90% Pb^{IV}.

Dibenzoyl peroxide (Harrington Laboratory Chemical) was washed with methanol and dried by suction. Copper(II) benzoate was prepared from copper(II) sulphate and sodium benzoate and was dehydrated by heating to 110° *in vacuo*. Copper(II) chloride (B.D.H. Laboratory Reagent) was the anhydrous material. Lithium acetate was Fisons Labora-

¹⁸ R. O. C. Norman and P. R. Storey, *J. Chem. Soc. (B)*, 1970, 1099.

¹⁹ C. R. E. Jefcoate and R. O. C. Norman, *J. Chem. Soc. (B)*, 1968, 48.

tory Reagent (hydrated) and was dehydrated as for copper(II) benzoate. All other reagents were as previously described.¹

The three methoxyphenyl benzoates were prepared from the phenol and benzoyl chloride. The isomeric methoxybiphenyls were prepared by the Gomberg reaction. Phenoxy-methylanisoles were kindly supplied by Professor H. B. Henbest. Phenoxy-methyl benzoate was prepared by heating phenoxy-methyl acetate¹ (5 g) with benzoic acid (50 g) at 180° for 60 h. Upon cooling, an ether solution of the mixture was washed with aqueous sodium hydrogen carbonate and dried (MgSO₄). Evaporation of the solvent gave a yellow oil (3.5 g) which crystallised on standing and gave a white solid, m.p. 36–37° [from light petroleum (b.p. 60–80°)] (lit.,⁹ 35–36°); τ 1.80–2.95 (10H, m, ArH) and 4.03 (2H, s, CH₂); *m/e* 228 (4%), 198 (14), 107 (3), 105 (100), 94 (3), and 77 (49), *m** 171.9 (228 → 198).

All other samples were commercially available, or were described in the preceding paper.¹

Oxidations.—Oxidations by lead tetrabenzoate followed the general procedures described for lead tetra-acetate in the preceding paper.¹ The results for competitive reactions were as follows.

(i) A mixture of anisole and benzene (4 ml; 1:1.16, w/w) with lead tetrabenzoate (0.4 g) and Perkadox (*ca.* 50 mg), under nitrogen at 80° for 10 min, gave biphenyl (12%), methoxybiphenyls (12%; *o:m:p* = 67:18:15), phenoxy-methyl benzoate (6%), and methoxyphenyl benzoates (65%; *o:p* = 29:71). A 0.1% yield of phenyl benzoate would have been detected.

(ii) A mixture of nitrobenzene and benzene (4 ml; 1.67:1, w/w) with lead tetrabenzoate (0.4 g) and Perkadox (*ca.* 50 mg), under nitrogen at 80° for 1 h, gave biphenyl (10%) and nitrobiphenyls (23%, *o:m:p* = 45:18:37).

The majority of the reactions with dibenzoyl peroxide were carried out by sealing the reaction solutions in ampoules (under nitrogen) and standing these in a bath at 80° for 60 h. Other reactions, the results of which are not fully described in the text, were as follows.

(i) Benzene (5 ml and 40 ml) and dibenzoyl peroxide (0.5 g) gave biphenyl (45 and 57%) and phenyl benzoate (2.6 and 2.7%).

(ii) Nitrobenzene (5 ml), copper(II) benzoate (0, 30, and 300 mg), acetic acid (0, 0, and 1 ml), and dibenzoyl peroxide (0.5 g) gave nitrobiphenyls (77%, *o:m:p* = 56:12:32; 72%, *o:m:p* = 59:11:30; and 52%, *o:m:p* =

57:12:31), along with biphenyl (*ca.* 1%) and phenyl benzoate (*ca.* 1%).

(iii) Mixtures of anisole and benzene (4 ml, 1:11:1 and 1:28:1, w/w), copper(II) benzoate (0 and 68 mg), and dibenzoyl peroxide (0.4 g) gave biphenyl (19 and 24%), methoxybiphenyls (33%, *o:m:p* = 72:12:16; and 33%, *o:m:p* = 64:20:16), phenyl benzoate (0.6 and 1.4%), methoxyphenyl benzoates (4 and 10%), phenoxy-methylanisoles (1 and 0%), and phenoxy-methyl benzoate (3 and 15%).

(iv) Anisole (5 ml), acetic acid (1 ml), copper(II) benzoate (0.5 g), and dibenzoyl peroxide (0.5 g) gave methylanisoles (2.5%), methyl benzoate (11%), phenoxy-methyl acetate (3%), methoxyphenyl acetates (8%, *o:p* = 35:65), methoxybiphenyls (3.5%, *o:m:p* = 63:19:18), phenoxy-methyl benzoate (1%), and methoxyphenyl benzoates (6%, *o:p* = 52:48).

(v) Anisole (5 ml), propionic acid (1 ml), and dibenzoyl peroxide (0.5 g) gave ethylanisoles (19%), phenoxy-methyl propionate (3%), methoxyphenyl propionates (0.2%), methoxybiphenyls (5%), phenoxy-methylanisoles (1%), phenoxy-methyl benzoate (1%), and methoxyphenyl benzoates (5%).

Reactions of dibenzoyl peroxide in acetonitrile as solvent with copper(II) chloride added were carried out as described by Kurz and his co-workers;^{3,20} the additional reagents (Table 7) were added after the other reagents had been mixed.

Reactions of dibenzoyl peroxide with benzene in the presence of lead(IV) were carried out as follows. A solution of the peroxide in benzene (20 ml) was degassed and brought to the reflux temperature under nitrogen. A degassed solution of the lead(IV) salt in benzene (20 ml) was added during 30 min. Heating was continued for a further 30 min, by which time no Pb^{IV} remained. No attempt was made to analyse for the amount of peroxide consumed. Lead tetrabenzoate (1.04 mmol) and peroxide (2.99 mmol) gave biphenyl (1.65 mmol) and phenyl benzoate (0.17 mmol). Lead tetra-acetate (1.01 mmol) and peroxide (2.34 mmol) gave biphenyl (0.98 mmol) and phenyl benzoate (0.14 mmol).

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[1/1445 Received, 12th August, 1971]

²⁰ M. E. Kurz and P. Kovacic, *J. Amer. Chem. Soc.*, 1967, **89**, 4960.