

Reactions of Lead(IV). Part XXVIII.¹ Oxidative Coupling of Methyl-substituted Benzenoid Compounds: Formation of Biaryls and Diarylmethanes in Trifluoroacetic Acid

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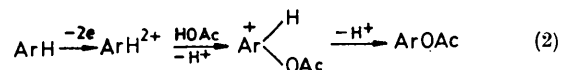
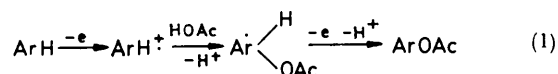
Methyl-substituted benzenes are oxidised readily at low temperatures by lead tetra-acetate in the presence of trifluoroacetic acid; the products are mainly biaryls and diarylmethanes, in proportions which vary markedly with the structure of the aromatic compound. Evidence has been adduced that the first step is the formation of an aromatic radical cation. This undergoes competitive reactions; it can react with another aromatic molecule to give ultimately a biaryl, and in this respect behaves as an electrophilic radical rather than as a cation, or it can undergo further oxidation to give a benzylic cation from which diarylmethanes are derived.

BENZENOID compounds can react with lead tetra-acetate in a variety of ways, depending on the structure of the compound and the conditions; among the types of products formed are those resulting from methylation, carboxymethylation, acetoxylation, plumbylation, and oxidative dimerisation. Three fundamental processes have been identified. The first is plumbylation, which has the characteristics of an S_E2 reaction.²⁻⁵ It occurs to a significant extent only when the aromatic compound is activated towards electrophilic reagents,²⁻⁴ it is reversible, and the resulting aryl-lead compounds can yield aryl cations⁵ and aryl radicals.^{3,4} The second process is formation of the methyl radical; this can be followed by aromatic methylation⁴ and, in the presence of acetic acid, by carboxymethylation, whence acetoxy-methyl derivatives can be derived.⁶ Finally, evidence has been adduced for an electron-transfer reaction involving the benzenoid compound as donor and lead(IV) as acceptor; the resulting electron-deficient aromatic ring can undergo nucleophilic attack by solvent or another aromatic molecule.^{3,5,7} This is the least well understood of the three processes and is the subject of this paper.

Our previous studies of the electron-transfer process have revealed the following. First, the order of reactivity amongst some aromatic compounds differs from that expected for S_E2 reactions. Second, less electron-rich benzenoid compounds react by electron transfer if reaction is carried out in trifluoroacetic acid.⁵ Third, the process can involve a peroxide-initiated chain reaction.⁷ This is compatible with a sequence involving one-electron transfer, nucleophilic attack, and a second one-electron oxidation [the ECE mechanism, in electrochemistry terminology; *e.g.*, reaction (1)] but not with a two-electron transfer followed by nucleophilic attack [the EEC mechanism, *e.g.* reaction (2)].

In the present work, we have studied the oxidation of methylated benzenes, both singly and in competition, by lead tetra-acetate in the presence of trifluoroacetic acid. The oxidant in trifluoroacetic acid was added

dropwise to a solution of the benzenoid compound(s) in dichloromethane which was stirred at 0°, and the mixture was allowed to warm to room temperature and worked up after 24 h; the benzenoid compound(s) were present



in large excess compared with the oxidant so as to minimise the occurrence of further oxidation of the products. In many instances the overall yields (based on lead tetra-acetate) were low, but in any case it was the relative amounts of products which were of significance. However, in some instances yields were high enough to give the method synthetic value; this was notably so in the case of some unsymmetrical diarylmethanes. Most of the products reported were isolated and fully characterised; those which were not isolated were identified by mass spectrometry following g.l.c. [in the cases of the biaryls (9), (19), (21), and (26) the position of attachment of the aryl rings could not be established with certainty (see Experimental section), but this is immaterial to the discussion of the *type* of oxidative coupling]. The results provide strong support for operation of the ECE mechanism and enable a number of characteristics of this type of reaction to be described.

RESULTS AND DISCUSSION

Oxidations.—*o*-Xylene gave the biaryls (1) (7%) and (2) (2%) and 3,4-xylene (11%); *m*-xylene gave the biaryl (3) (23%) and 2,4-xylene (24%). In contrast, *p*-xylene gave mainly two diarylmethanes, (5) (18%) and (6) (4%), together with 2,5-xylene (13%) and only a trace of the biaryl (4).

The oxidation of equimolar amounts of benzene and *p*-xylene gave essentially the same products as *p*-xylene alone; there were traces (<0.5%) of phenyl-*p*-tolylmethane and phenol. Likewise, equimolar amounts of

¹ Part XXVII, A. Lethbridge, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 1973, 35.

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

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

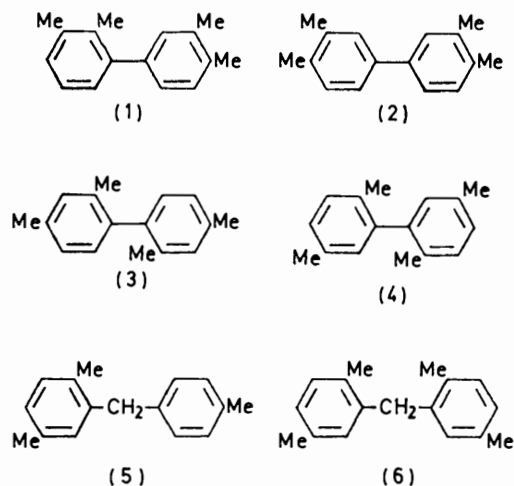
⁴ D. R. Harvey and R. O. C. Norman, *J. Chem. Soc.*, 1964, 4860.

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

⁶ E. I. Heiba, R. M. Dessau, and W. J. Koehl, jun., *J. Amer. Chem. Soc.*, 1968, **90**, 1082.

⁷ R. A. McClelland, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 1972, 562.

p-xylene and chlorobenzene or nitrobenzene gave only the products formed by *p*-xylene; no diarylmethane involving the other aromatic compound was detected. However, when equimolar amounts of *p*-xylene and anisole were oxidised, the main products were derived



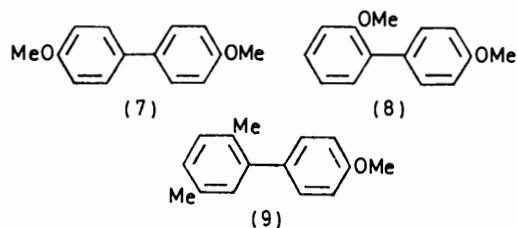
from anisole; the biaryls (7)–(9) were produced in relative amounts 2.8 : 2.3 : 1, and there was only a trace of the diarylmethane (5). The oxidation of *p*-xylene was also carried out with lead tetra-acetate which had been scrupulously freed from acetic acid and with samples of this material to which known amounts of acetic acid had been added; as the results in Table 1 show, a high yield of the diarylmethane (5) can

TABLE 1

Products (mol %) from the oxidation of *p*-xylene (0.16 mol) with lead tetra-acetate (2.6×10^{-3} mol) in trifluoroacetic acid (0.13 mol) and dichloromethane (30 ml)

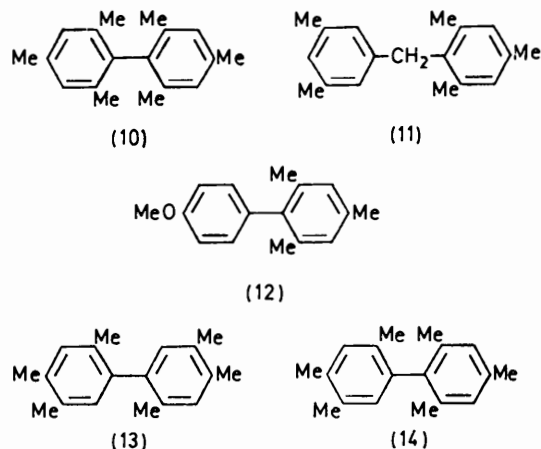
HOAc added (ml)	Products			
	2,5-Xylenol	(4)	(5)	(6)
0	16	1.5	73	6
1	23	1.8	41	8
3	28	1.7	18	3
5	35	0.9	13	0.7
8	38	0.5	6	0.1

be obtained under the former conditions but it falls rapidly as the amount of acetic acid increases, partly because of the more efficient formation of 2,5-xylenol.

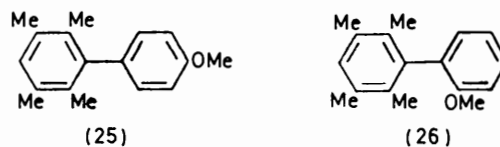
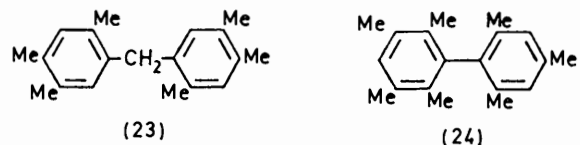
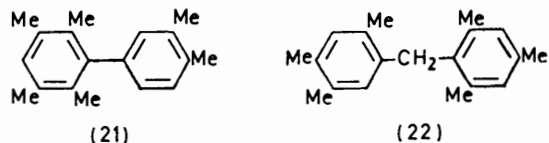
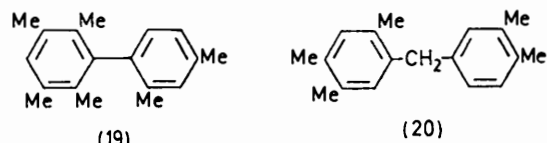
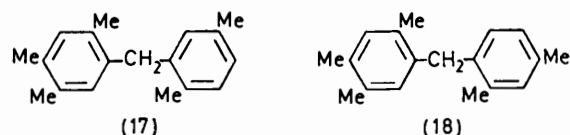
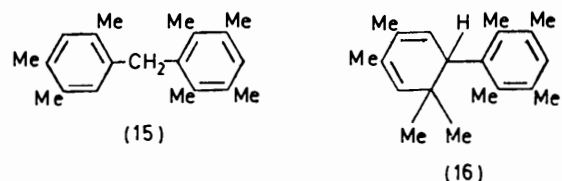


The oxidation of mesitylene gave bimesityl (10) in 65% yield, with traces of mesitol and the diarylmethane (11). Bimesityl was again essentially the only product when equimolar amounts of mesitylene and either benzene or *p*-xylene were oxidised, but equimolar

amounts of mesitylene and anisole gave mainly the biaryl (12) (2.5 parts) and 2,4'- and 4,4'-dimethoxybiphenyl (1 part), with only a trace of bimesityl.

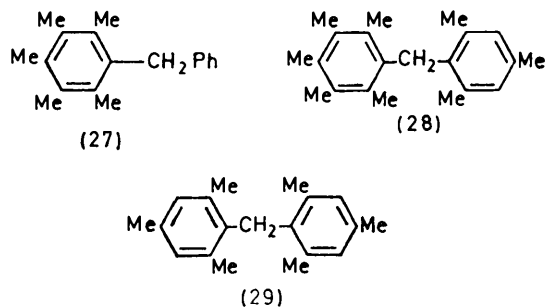


Pseudocumene gave the biaryl (13) as the major product, with traces of isomeric pentamethyldiphenylmethanes; when oxidised with an equimolar amount of mesitylene, it gave the biaryls (14), (13), and (10) in relative amounts 4.0 : 2.7 : 1.



Durene gave the diarylmethane (15) in 60% yield; there were traces of durol and 2,4,5-trimethylbenzyl acetate, but no biduryl was detected. When acetic acid was included in the solvent, the diarylmethane was still the dominant product, but yields of the other two derivatives were slightly increased and there was a small quantity of a material tentatively identified (mass spectroscopy) as (16). When durene and a five-fold excess of *p*-xylene were oxidised, the diarylmethanes (17), (15), and (5) were formed in relative amounts 10:10:1; durene and a five-fold excess of *m*-xylene gave the products (18), (19), (15), and (3) in relative amounts 50:16:4:1; and durene and a five-fold excess of *o*-xylene gave the products (20), (21), and (15) (3:1:2:1), together with traces of the biaryls (1) and (2). Equimolar amounts of durene and mesitylene gave mainly the diarylmethane (22) (65%), together with the diarylmethanes (15) (8%) and (23) (3%) and the biaryls (24) (7%) and (10) (1%). Equimolar amounts of durene and anisole gave the biaryls (25) and (26) (15:1) and traces of the diarylmethane (15) and 2,4'- and 4,4'-dimethoxybiphenyl. An equimolar mixture of durene, mesitylene, and anisole gave the biaryls (25) and (12) (3:2:1), with traces of the diarylmethane (15) and the two dimethoxybiphenyls.

When hexamethylbenzene was oxidised together with a twenty-fold excess of benzene, the diarylmethane (27) was obtained, and oxidation with a five-fold excess of mesitylene gave the diarylmethanes (28) and (29) and bimesityl (10) (30:16:1), with traces of products the g.l.c. retention times of which were the same as those of pentamethylbenzene and the tetramethylbenzenes.



Mechanisms of Oxidation.—Of the benzenoid compounds we have studied, three (*p*-xylene, durene, and hexamethylbenzene) yield species which are capable of effecting aromatic arylmethylation. The remainder yield mainly biaryls and (especially for the xylenes) phenols.

We considered four possible mechanisms for the production of biaryls: the formation and then fragmentation of an aryl-lead species, and aromatic substitution by the resulting aryl radical or cation; formation of an aromatic radical cation, union of two such species, and the loss of two protons; formation of a dication followed by substitution in another aromatic molecule (EEC

mechanism); and formation of a radical cation followed by its reaction with another aromatic molecule and then a further one-electron oxidation (ECE mechanism).

The first possibility is unlikely for several reasons. First, an aryl-lead compound, if formed, is unlikely to undergo homolysis at a significant rate at the temperature employed,^{3,4} although it might undergo heterolysis.⁵ Second, the selectivity apparent from, for example, the formation of (3) as the sole biaryl from *m*-xylene, or of bimesityl from a mixture of mesitylene and benzene, is compatible neither with attack by an aryl radical nor with the behaviour expected of an especially unselective aryl cation.^{5,8} Third, from their known susceptibilities to electrophilic attack,⁹ one would expect *p*-xylene and durene to react by way of plumblylation, as well as *o*-xylene and mesitylene; if steric hindrance from two *ortho*-methyl substituents were to prevent plumblylation of durene, it might also be expected of mesitylene.

The second possibility is rendered improbable by the results for the oxidations of arene mixtures which give one or more biaryls. Consider the oxidation of such a mixture in which one component, ArH, yields its radical cation α times as fast as the other component, Ar'H. Then, if the rates of coupling do not differ significantly for the three possible pairings ($2\text{ArH}^{\cdot+}$; $\text{ArH}^{\cdot+} + \text{Ar}'\text{H}^{\cdot+}$; $2\text{Ar}'\text{H}^{\cdot+}$), the biaryls will be formed in relative yields $\alpha^2:2\alpha:1$ for ArAr, ArAr', and Ar'Ar'. However, in the following five cases the yield of the unsymmetrical biaryl(s) is greater than can be accounted for in this way: mesitylene and anisole, mesitylene and pseudocumene, mesitylene and durene, durene and anisole, durene and *m*-xylene. In addition, if the production of the unsymmetrical biaryls formed by reaction of durene with *m*-xylene and with mesitylene (in greater yields than the bixylenyl and bimesityl) were to involve the durene radical cation, it would be hard to understand the absence of biduryl in these cases and when durene is oxidised alone.

The EEC mechanism is unlikely in view of the behaviour of mixtures of anisole with mesitylene and with durene. If the source of the methoxyphenyl-containing biaryls in each case was the dication PhOMe^{2+} , then we should expect the dimethoxybiphenyls to predominate over the monomethoxybiaryls,* contrary to observation.

The ECE mechanism is, we believe, the correct description of the reaction. It is discussed in detail later, and we note here that the objections to the other possible modes of reaction do not apply to this mechanism. Thus, the formation of an arylmethylating species from a methylbenzene can succeed formation of the radical cation; the reasonable degree of selectivity in biaryl formation can be attributed to the fact that the radical cations, while behaving essentially as radicals in their aromatic homolytic substitutions, are nevertheless,

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

* R. O. C. Norman and R. Taylor, 'Electrophilic Substitution in Benzenoid Compounds,' Elsevier, Amsterdam, 1965.

* For example, the relative reactivities towards bromine of anisole (*para*-position), mesitylene, and durene are $10^4:10^3:1$.

by virtue of their positive charge, strongly electrophilic and consequently discriminating ones; and the predominance in many cases of unsymmetrical over symmetrical biaryls can be understood in terms of there being two crucial steps in the process—excitation of one aromatic molecule and its homolytic substitution in another—and the orders of effectiveness amongst a group of reactants in the two steps are not necessarily the same.

The results of oxidations of mixtures of two compounds yield information directly about the relative ease both of the formation of the two radical cations and of arylation of each aromatic substrate by a radical cation. Thus, the products from the following mixtures show that the first member in each pair is more reactive than the second in both forming and reacting with a radical cation: *p*-xylene and benzene; anisole and *p*-xylene; mesitylene and benzene; mesitylene and *p*-xylene. However, in other cases the situation is not clear. For example, the greater yield of the unsymmetrical biaryl (14) than of the symmetrical biaryls (13) and (10) from a mixture of pseudocumene and mesitylene could be accounted for either by pseudocumene's being more reactive than mesitylene in yielding the radical cation and less reactive in reacting with a radical cation, or *vice versa*.

This difficulty applies also to the results from mixtures of anisole with mesitylene and with durene, but in this case further progress can be made by considering the results of oxidation of a mixture of all three compounds, where the main products were the unsymmetrical biaryls (25) and (12) (3.2 : 1) and there were traces of dimethoxybiphenyls. This could be accounted for in two ways: either durene is oxidised to its radical cation about three times as fast as is mesitylene and far more rapidly than is anisole, and the radical cations from durene and mesitylene each react preferentially with anisole; or anisole is the most readily oxidised of the three and its radical cation reacts with the aromatic compounds in the order durene > mesitylene > anisole. Now, the oxidation of a mixture of durene and mesitylene shows that the former is oxidised to a reactive intermediate at least nine times as rapidly as is the latter; further, when oxidised either alone or with *p*-xylene, durene provides exclusively an arylmethylating agent, and when oxidised with mesitylene or *o*- or *m*-xylene it yields at least mainly an arylmethylating agent (moreover, the relatively small yields of duryl-containing biaryls in these cases could arise *via* the radical cation from the co-reactant). The first possibility is therefore unlikely, but the data are consistent with the alternative suggestion. The result of oxidation of durene and mesitylene can be interpreted in terms of the more rapid reaction of the former with the oxidant, giving ultimately diaryl-methanes *via* further oxidation of the durene radical cation, with the slower oxidation of mesitylene to its radical cation being followed by arylation of both

durene and mesitylene, the former the more rapidly. We therefore suggest the following order for relative rates of oxidation to reactive intermediates: anisole > durene > mesitylene > *p*-xylene > benzene (the position of pseudocumene is considered later) and the following for the relative ease of arylation by a radical cation: durene > mesitylene > anisole > *p*-xylene > benzene.

Relative ease of oxidation. The order for relative rates of oxidation can be compared with those for other processes involving the loss, or incipient loss, of an electron from the aromatic compound. The data in Table 2 are concerned with four such processes: gas-

TABLE 2

Measures of the ease of removal of one electron from some benzenoid compounds

Benzenoid compound	I.P. ^a /eV	ν_{\max} , ^b /cm ⁻¹	K °/ kg mol ⁻¹	Relative rates ^d
Durene	8.03	17,200	4.9	275
Anisole	8.22	18,100		
Pseudocumene	8.27		2.5	20
Mesitylene	8.39	19,600	2.2	5.7
<i>p</i> -Xylene	8.45	19,600	1.5	5.2
Benzene	9.25	24,600	0.7	1

^a Ionisation potential.¹⁰ ^b Lowest energy absorption maxima for complexes with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone.¹¹ ^c Association constants for complexes with fluoranil.¹¹ ^d Relative rates of oxidation by cobalt(III) acetate in the presence of chloride ion.¹²

phase ionisation potentials,¹⁰ the lowest energy absorption maxima for charge-transfer complexes formed with a quinone as acceptor,¹¹ association constants for the charge-transfer complexes formed with fluoranil,¹¹ and relative rates of oxidation by cobalt(III) in which one-electron transfer is believed to be the rate-determining step.¹² The orders are the same except, for our oxidations, that we have been unable to place pseudocumene in the sequence and that anisole is more, not less, reactive than durene.

On the basis of this comparison, we suggest that our results for oxidation of a mixture of pseudocumene and mesitylene reflect the greater ease of oxidation of the former and slightly greater susceptibility to arylation of the latter. The greater reactivity of anisole than durene might result from co-ordination of its oxygen atom to lead(IV), providing a kinetically more favourable path for electron transfer than is available to the methylbenzenes; alternatively, it may be that the methyl substituents in durene hinder the approach of the oxidant to the molecular π -system.

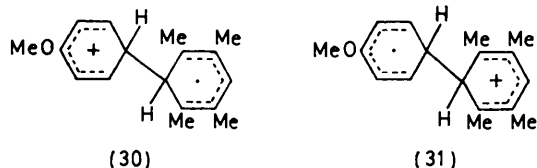
Relative ease of arylation. The reaction of an aromatic radical cation with another benzenoid molecule is expected to lead to an intermediate in which one ring bears an unpaired electron and the other a positive charge. Two possibilities are available, as illustrated for the reaction of the anisole radical cation with durene to give the biaryl (25); the radical cation could act as a radical, to give the intermediate (30), or as a cation to

¹⁰ R. Foster, 'Organic Charge-Transfer Complexes,' Academic Press, London and New York, 1969.

¹⁰ R. W. Kiser, 'Introduction to Mass Spectrometry and its Applications,' Prentice-Hall, New Jersey, 1965.

¹² E. I. Heiba, R. M. Dessau, and W. J. Koehl, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 6830.

give the intermediate (31).^{*} If the latter were the case, then, since anisole is more reactive than durene to electrophilic reagents,⁹ we should expect the dimethoxybiphenyls to be formed in higher yield than the biaryl (25) from a mixture of anisole and durene, in contrast to observation. However, the result is consistent with the former possibility since durene is more reactive than anisole towards free radicals.¹⁴ Therefore, at least in this instance, we infer that the radical cation acts as a radical. A similar argument suggests that this is also the case in the reaction of the anisole radical cation with mesitylene. Moreover, although we cannot be certain that it is generally true, we suspect it to be so in all the reactions we have described in which biaryls are formed; we note that, on this assumption, each intermediate (and thus the rate-determining transition state) in biaryl formation is described by a structure in which the positive charge is stabilised by *p*-Me, whereas, when it cannot be so stabilised, arylation is less effective than arylmethylation. [We note, too, that, as judged by the relative yields of compounds (25) and (26), the anisole radical cation has a strong preference for arylation by way of its *para*-position.]

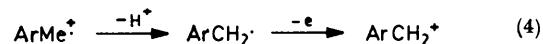
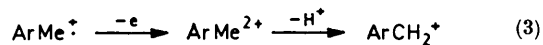


Arylmethylation. The results from the competitive experiments show that, towards the arylmethylating agent from *p*-xylene, *p*-xylene is more reactive than benzene; and comparison of the yields of the diarylmethane (15) from durene with those formed by the arylmethylating species from durene with other benzenoid compounds (making allowance for the excess of one of the two compounds in some cases) gives the following measure of relative reactivities towards this species: mesitylene : *m*-xylene : durene : *o*-xylene : *p*-xylene \equiv 8 : 2.5 : 1 : 0.6 : 0.2.

This order is that for substitution of the compounds by electrophilic reagents,^{9,15} and the relatively small numerical scale is consistent with electrophilic arylmethylation by a species of comparatively low selectivity, as in the case for benzylation by benzyl bromide in the presence of gallium tribromide.¹⁵ We infer that the arylmethylating agent is a free or incipient arylmethyl cation. The cation could be formed from the aromatic radical cation by either reaction (3) or (4); we cannot distinguish between these paths but note that the latter is more likely on energetic grounds and that the absence of 1,2-diarylethanes, from dimerisation of the species ArCH_2^{\cdot} , does not exclude this reaction since we should

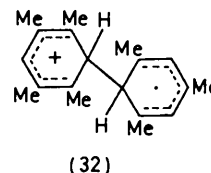
^{*} We should not necessarily expect (30) and (31) to be descriptive structures of the same delocalised system since the two conjugated units are insulated from each other; for example, e.s.r. studies have shown that the unpaired electron in the radical anion $\text{O}_2\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NO}_2^{\cdot-}$ is essentially located at one nitro-group.¹³

expect such radicals to undergo rapid one-electron oxidation under the reaction conditions.



There remains the problem of why *p*-xylene and durene behave preferentially as arylmethylating agents, whereas toluene,⁵ the other xylenes, mesitylene, and pseudocumene act as arylating agents. We considered first the possibility that *p*-xylene and durene are exceptional simply because they yield arylmethyl cations more readily than other members of the group. For durene, we might expect this to be so because, as judged from the order of first ionisation potentials, durene is likely to form an aromatic dication the most readily of the series. However, for *p*-xylene, we should not expect the energy required to remove two electrons to be less than that for pseudocumene (in which there is not only the *para*-disposition of cation-stabilising methyl groups which is present in *p*-xylene but also a third stabilising methyl group); likewise, an explanation in terms of the greater stability—and thus more rapid formation—of the *p*-methylbenzyl cation from *p*-xylene, compared with the corresponding cations from toluene, *o*- and *m*-xylene, and mesitylene, based on the stabilising influence of *p*-Me, is unlikely since an arylmethyl cation formed from pseudocumene at either the 1- or the 4-position would be stabilised by both *p*-Me and a second Me substituent.

It is notable that *p*-xylene and durene are the only two compounds in the series the radical cations from which, if they act as radicals in arylation, give intermediates lacking a *p*-Me substituent for the stabilisation of the positive charge; for example, the intermediate for the arylation of mesitylene by the durene radical cation would be (32). We therefore suggest that the factors determining the relative tendencies for occurrence of arylation and arylmethylation come into operation after the aromatic radical cation has been formed; if this species can yield an arylation intermediate the positive charge in which is stabilised by *p*-Me or *p*-OMe, it does so, but otherwise the activation parameters are such that reaction (3) or (4) occurs in preference and the major products are diarylmethanes.



Formation of other products. As well as the products we have discussed, products of three other types were

¹³ D. J. Edge, R. O. C. Norman, and P. M. Storey, *J. Chem. Soc. (B)*, 1970, 1096; see also J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, 1963, **39**, 778.

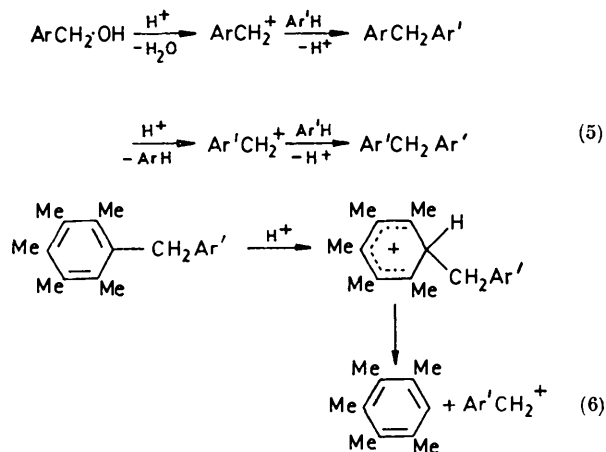
¹⁴ G. H. Williams, 'Homolytic Aromatic Substitution, Pergamon, Oxford, 1960.

¹⁵ L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, **1**, 35.

obtained, often in only small yield. These were: (i) phenols; (ii) the diarylmethanes (6) and (29) in which an extra methylene group has been incorporated to join the two arenes concerned; (iii) products in which a methyl group has been removed from an aromatic ring, namely (23) from durene and mesitylene, and pentamethylbenzene from hexamethylbenzene and mesitylene.

(i) The phenols are likely to be formed from aryl trifluoroacetates during work-up;⁵ control experiments showed that aryl acetates are not hydrolysed under these conditions. They were significant products only with the xylenes, which are the least reactive compounds of those we have studied here in terms of their ability to release one electron. It is therefore probable that, in these cases, reaction occurs by way of charge-transfer complexes with the oxidant (*i.e.* partial electron transfer) which can rearrange to the trifluoroacetoxylation intermediate, and/or *via* electrophilic plumblylation followed by the replacement of the lead substituent by trifluoroacetoxy;⁵ the latter is especially likely to be the case for those reactions of *p*-xylene in which acetic acid was added, since our previous results show that this depresses the ease of electron transfer from a benzenoid compound more effectively than the ease of plumblylation.⁵

(ii) It has been shown¹⁶ that pentamethylbenzyl alcohol, ArCH_2OH , and its derivatives react with an aromatic compound $\text{Ar}'\text{H}$ in the presence of sulphuric acid to yield pentamethylbenzene and the diarylmethane, $\text{Ar}'\text{CH}_2\text{Ar}'$; it was suggested that the process occurs as in reaction (5), the acid-induced heterolysis of the intermediate $\text{ArCH}_2\text{Ar}'$ being promoted by the relief of steric crowding, reaction (6).



The formation of the diarylmethanes (6) and (29) may occur in a similar manner; the former could arise from (5) by way of the 2,5-dimethylbenzyl cation and more *p*-xylene, and the latter from (28), by way of the 2,4,6-trimethylbenzyl cation and more mesitylene.

(iii) The last reaction gives pentamethylbenzene in

¹⁶ H. Suzuki and K. Nakamura, *Bull. Chem. Soc. Japan*, 1968, **41**, 2197.

¹⁷ K. Nyberg, *Acta Chem. Scand.*, 1970, **24**, 1609.

¹⁸ P. Kovacic and C. Wu, *J. Org. Chem.*, 1961, **28**, 759, 762.

¹⁹ P. Kovacic and A. K. Sparks, *J. Org. Chem.*, 1963, **28**, 972.

addition to (29) and can therefore account for this demethylated product. The diarylmethane (22) could give pseudocumene and the mesitylmethyl cation with acid, reaction of the former with the arylmethyl cation from durene leading to (23).

Comparison with other reactions. The courses of the reactions we have described closely resemble those which occur during anodic oxidation in dichloromethane. Under these conditions, mesitylene gives more bimesityl than diarylmethanes whereas durene gives mainly the diarylmethane (15) but no biduryl and *p*-xylene gives more diarylmethanes than biaryl; it has been suggested that the diarylmethanes are formed by loss of two electrons from the aromatic ring, and that the biaryls originate from aromatic radical cations.¹⁷ There is also a close similarity to reactions of methylated benzenes with iron(III) chloride or antimony pentachloride;^{18,19} for example, with the former reagent, *m*-xylene and mesitylene yield, *inter alia*, the biaryls (3) and (10), respectively, whereas *p*-xylene yields a triarylmethane and the diarylmethanes (5) and (6). It is notable, too, that durene with nitric acid gives, *inter alia*, the diarylmethane (15) whereas hemimellitene gives a biaryl;²⁰ the suggestion has been made that the former reaction involves the addition of nitronium ion followed by the loss of a proton and nitrite ion to give the (incipient) 2,4,5-trimethylbenzyl cation.²⁰ Two other oxidants, cobalt(III)^{12,21} and manganese(III),²² are thought to react with benzenoid compounds by forming aromatic radical cations; these reactions have usually been carried out in the presence of reasonably strong nucleophiles, such as acetic acid,^{12,22} which trap the intermediates from the aromatic compounds, and this doubtless accounts for the differences in products from those under our conditions.

EXPERIMENTAL

The analytical methods and many of the materials used have been described.⁵ The stationary phases for g.l.c. were diethylene glycol adipate polyester (DEGA) and silicone oil SE30; preparative g.l.c. was performed on a Pye instrument (Series 105). The methylbenzenes were available commercially.

Reference Compounds.—2,5-Dimethylphenyl acetate was prepared by adding acetic anhydride (10 ml) to 2,5-xyleneol (12 g) in 3M-sodium hydroxide (150 ml) containing ice (100 g), shaking for 10 min, and washing (dilute NaOH) and drying (MgSO_4) the ether extract; evaporation of the solvent and distillation gave the ester, b.p. 223–226° at 743 mmHg (lit.,²³ 224° at 741 mmHg); τ (CCl_4) 2.95–3.25 (3H, m, ArH), 7.73 (3H, s, Me), 7.85 (3H, s, Me), and 7.94 (3H, s, Me). *p*-Methylbenzyl acetate, from acetyl chloride (5 ml) and *p*-methylbenzyl alcohol (6 g) in glacial acetic acid (15 ml) (heated for 1 h at 100° after the exothermic reaction had subsided, and then fractionated) had b.p. 227°

²⁰ S. B. Hanna, E. Hunziker, T. Saito, and H. Zollinger, *Helv. Chim. Acta*, 1969, **52**, 1537.

²¹ R. M. Dessau, S. Shih, and E. I. Heiba, *J. Amer. Chem. Soc.*, 1970, **92**, 412.

²² P. J. Andrulis, jun., M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Amer. Chem. Soc.*, 1966, **88**, 5473.

²³ Beilstein's Handbuch, Band 6, II, 467.

(lit.,²⁴ 227—230°); τ (CCl₄) 2.90 (4H, s, ArH), 5.07 (2H, s, CH₂), 7.71 (3H, s, Me), and 8.05 (3H, s, Me).

Diarylmethanes. Bis-2,5-dimethylphenylmethane (6) was prepared from *p*-xylene and formaldehyde in the presence of sulphuric acid;²⁵ it was obtained, after chromatography on alumina with light petroleum, as crystals, m.p. 59—61° (from ethanol) (lit.,²⁵ 61—62°); τ 2.90—3.00 (4H, m, ArH), 3.25 (2H, s, ArH), 6.16 (2H, s, CH₂), and 7.79 (12H, s, Me). 2,5-Dimethylphenyl-(2,4,5-trimethylphenyl)methane (17) was prepared by adding titanium tetrachloride (1 ml) to 2,5-dimethylbenzyl chloride (7.5 g) in pseudocumene (100 ml) at 0°, heating for 1 h at 100° after the initial exothermic reaction, and pouring into water; it was obtained, following extraction into ether, washing (dilute NaOH), drying, and evaporation, as a solid, m.p. 69.5—70° (from methanol) (Found: C, 90.8; H, 9.3. C₁₈H₂₂ requires C, 90.7; H, 9.3%); τ 3.02 (1H, s, ArH), 3.07 (2H, s, ArH), 3.31 (1H, s, ArH), 3.35 (1H, s, ArH), 6.22 (2H, s, CH₂), 7.81 (9H, s, Me), 7.84 (3H, s, Me), and 7.88 (3H, s, Me). Bis-2,4,5-trimethylphenylmethane (23) was prepared from pseudocumene and formaldehyde in the presence of toluene-*p*-sulphonic acid,²⁶ and was obtained, after distillation *in vacuo* from the tarry residue, as crystals, m.p. 93.5—94.5° (from light petroleum) (lit.,²⁷ 94—95°); τ 3.05 (2H, s, ArH), 3.32 (2H, s, ArH), 6.21 (2H, s, CH₂), 7.82 (12H, s, Me), and 7.87 (6H, s, Me). A similar reaction, with mesitylene in place of pseudocumene, gave bis-2,4,6-trimethylphenylmethane (29), m.p. 132—135° (from methanol-benzene) (lit.,²⁵ 134—135°); τ 3.22 (4H, s, ArH), 6.02 (2H, s, CH₂), 7.78 (6H, s, Me), and 7.94 (12H, s, Me). The biaryl (4) and the diarylmethanes (5) and (11) were obtained from oxidations with palladium(II) acetate which will be described subsequently.²⁸

The following compounds were identified by mass spectroscopy following g.l.c. The biaryl (9) had *m/e* 212 (*M*⁺, 100%), 197 (16), 182 (8), 154 (7), 153 (7), 152 (8), 107 (5), and 77 (6). Its retention time on g.l.c. was much shorter than those of methoxy-substituted 4-methyl-diphenylmethanes, and the latter all show strong ions of *m/e* 105 and 121. The compound is therefore deduced to be a 2,5-dimethylbiphenyl, and analogy with the major products, (12) and (25), of similar oxidations suggests that the methoxy-substituent is at the 4'-position. The product tentatively identified as (16) had *m/e* 268 (*M*⁺, 100%), 253 (19), 239 (8), 238 (12), 237 (8), 223 (8), 150 (6), and 146 (6). 2,4-Dimethylphenyl-(2,4,5-trimethylphenyl)-methane (18) had *m/e* 238 (*M*⁺, 83%), 223 (100), 208 (18), 193 (25), 132 (62), 118 (98), and 91 (20). Cleavage of the benzylic link accompanied by hydrogen transfer (peaks *m/e* 132 and 118 in this case) is a characteristic fragmentation mode of diphenylmethanes which possess a methyl substituent at the 2-position;²⁹ since the same compound was obtained by the oxidation of pseudocumene with palladium(II) acetate,²⁸ the diphenylmethane can only have structure (18). The biaryl (19) had *m/e* 238 (*M*⁺, 98%), 223 (100), 209 (13), 208 (33), 207 (21), 193 (31), 192 (15), 191 (12), 179 (11), 178 (13), and 165 (11). The absence of significant peaks at *m/e* 132 and 146 shows that the compound is not an (*o*-methyl)diphenylmethane, and of the three possible

biaryls from durene and *m*-xylene, the most probable is (19) by analogy with the formation of compound (3). 3,4-Dimethylphenyl-(2,4,5-trimethylphenyl)methane (20) had *m/e* 238 (*M*⁺, 49%), 223 (100), 208 (14), 193 (19), 132 (35), and 91 (12). The presence of *m/e* 132 and the absence of significant peaks at *m/e* 118 and 146 shows that the compound is a diphenylmethane with only one nucleus containing a methyl group *ortho* to the benzylic link, that nucleus bearing two other methyl substituents; only structure (20) is compatible with this evidence and the nature of the starting materials, and moreover the same compound was obtained from pseudocumene and palladium(II) acetate.²⁸ The biaryl (21) had *m/e* 238 (*M*⁺, 95%), 223 (100), 209 (18), 208 (43), 207 (20), 193 (33), 179 (13), 178 (14), and 165 (15). The absence of peaks at *m/e* 118, 132, and 146 shows that the compound is not an (*o*-methyl)-diphenylmethane, and of two possible biaryls from durene and *o*-xylene, (21) is the more likely on steric grounds. 2,2',3,4',5,6,6'-Heptamethylbiphenyl (24) had *m/e* 252 (*M*⁺, 100%), 237 (57), 222 (17), 221 (11), and 207 (21). The absence of peaks at *m/e* 132 and 146 shows that it is not an (*o*-methyl)diphenylmethane, and durene and mesitylene can form only one biaryl, namely (24), to which the spectrum is assigned. The biaryl (26) had *m/e* 240 (*M*⁺, 100%), 225 (62), 211 (17), 210 (31), 209 (28), 195 (25), 193 (17), 179 (17), 178 (17), and 165 (23). This is a similar spectrum to that of the biaryl (25), and analogy with the products from the oxidation of anisole alone suggests that the compound is the 2'-OMe isomer of (25).

Oxidations.—(a) *The xylenes.* A solution of lead tetraacetate (4.3 g) in trifluoroacetic acid (30 g) was added dropwise to a solution of *m*-xylene (20 ml) in dichloromethane (20 ml) at 0°, with stirring. A deep red colour formed and next day the solution was poured into water; the ether extract (2 × 250 ml) was shaken with *m*-sodium hydroxide (300 ml). The aqueous solution was acidified (2*M*-HCl) and neutralised (NaHCO₃), and its ether extract was combined with the previous extract, dried, and evaporated to ca. 50 ml for g.l.c. followed by mass spectrometry; analysis of xylenol was performed on DEGA (180°) and that of biaryls on silicone oil (200°), with biphenyl as internal standard. Removal of phenolic compounds from the product mixture by extraction of the ether solution with dilute sodium hydroxide, followed by preparative g.l.c. of the remainder, gave 2,2',4,4'-tetramethylbiphenyl (3), m.p. 38—39° (from methanol) (lit.,¹⁸ 40—41°), τ (CCl₄) 3.0—3.15 (6H, m, ArH), 7.70 (6H, s, Me), and 8.04 (6H, s, Me).

Reactions with *o*- and *p*-xylene, including work-up and analysis, were carried out in the same way; after addition of the oxidant, the solutions became, respectively, purple and dark orange. Preparative g.l.c. of the product from *o*-xylene gave 2,3,3',4'-tetramethylbiphenyl (1), m.p. 45—46° (from methanol) (lit.,³⁰ 45—46°); τ (CCl₄) 3.03 (6H, s, ArH), 7.73 (9H, s, Me), and 7.91 (3H, s, Me); and 3,3',4,4'-tetramethylbiphenyl (2), m.p. 73—74° (from methanol) (lit.,³¹ 73—75°); τ (CCl₄) 2.65—2.94 (6H, m, ArH) and 7.74 (12H, s, Me).

²⁸ R. O. C. Norman, C. B. Thomas, and J. S. Willson, unpublished observations.

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²⁴ G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.*, 1954, 3943.

²⁵ C. M. Welch and H. A. Smith, *J. Amer. Chem. Soc.*, 1951, **73**, 4391.

²⁶ J. G. Hendrickson and F. T. Wadsworth, *Ind. Eng. Chem.*, 1958, **50**, 877.

²⁷ H. Suzuki, *Bull. Chem. Soc. Japan*, 1969, **42**, 2618.

Reactions of equimolar mixtures of *p*-xylene and a second benzenoid compound were carried out in the same way. Those described in Table 1 were with a sample of lead tetra-acetate more thoroughly freed of acetic acid⁵ to which measured amounts of acetic acid were added.

(b) *Mesitylene*. A solution of lead tetra-acetate (1.67 g) in trifluoroacetic acid (32.9 g) was added dropwise to a solution of mesitylene (30 ml) in dichloromethane (20 ml) at 0°, with stirring. The resulting deep red solution was worked up next day as in (a) and evaporated to *ca.* 5 ml. Highly coloured materials were removed by boiling a solution in ethanol (20 ml) with charcoal, and the filtered solution, on cooling in a methanol–solid carbon dioxide bath, deposited bimesityl (10) (0.52 g), m.p. 100–101° (from ethanol) (lit.,³² 102–102.5°); τ 3.05 (4H, s, ArH), 7.68 (6H, s, Me), and 8.15 (12H, s, Me). A mixture of mesitylene (13.8 g) and anisole (12.3 g) was oxidised similarly, with lead tetra-acetate (1.65 g) in trifluoroacetic acid (13.5 g). The green solution was worked up as before, and preparative g.l.c. gave crystals of 2,4,6-trimethyl-4'-methoxybiphenyl (12), m.p. 74–75° (from methanol) (Found: C, 85.0; H, 8.0. C₁₆H₁₈O requires C, 84.9; H, 8.0%); τ (CCl₄) 3.13 (4H, s, ArH), 3.25 (2H, s, ArH), 6.25 (3H, s, OMe), 7.76 (3H, s, Me), and 8.07 (6H, s, Me).

(c) *Pseudocumene*. Pseudocumene (50 ml) was oxidised as in (b), with lead tetra-acetate (4 g) and trifluoroacetic acid (30 g), and quantitative analysis was performed as in (a). Preparative g.l.c. gave 2,2',4,4',5,5'-hexamethylbiphenyl (13), m.p. 51–53° (lit.,³³ 52°); τ (CCl₄) 3.20 (2H, s, ArH), 3.33 (2H, s, ArH), 7.82 (12H, s, Me), and 8.10 (6H, s, Me).

A mixture of pseudocumene (20 ml) and mesitylene (20 ml) was oxidised as in (b), with lead tetra-acetate (9 g) in trifluoroacetic acid (45 g). The golden yellow solution was worked up as before, and preparative g.l.c. gave 2,2',4,4',5,6'-hexamethylbiphenyl (14) as crystals, m.p. 43–46° (Found: C, 90.7; H, 9.4. C₁₈H₂₂ requires C, 90.7; H, 9.3%); τ (CCl₄) 3.11 (1H, s, ArH), 3.26 (2H, s, ArH), 3.35 (1H, s, ArH), 7.76 (3H, s, Me), 7.80 (6H, s, Me), and 8.15 (9H, s, Me).

(d) *Durene*. Durene (8.3 g) in dichloromethane (30 ml) was oxidised as in (a), with lead tetra-acetate (7.1 g) in trifluoroacetic acid (38 g). The yellow solution was worked up next day and analysed as in (a); quantitative determination was performed on the silicone column (200°) with bibenzyl as internal standard. Highly coloured material and excess of durene were removed by chromatography on alumina in light petroleum, to give 2,3,5,6-tetramethylphenyl-(2,4,5-trimethylphenyl)methane (15), m.p. 158–160° (from light petroleum) (lit.,¹⁷ 160–162°); τ 3.09 (2H, s, ArH), 3.76 (1H, s, ArH), 6.16 (2H, s, CH₂), 7.68 (3H, s, Me), 7.78 (6H, s, Me), 7.85 (3H, s, Me), and 7.98 (9H, s, Me).

The oxidation of durene in the presence of a five-fold excess of a xylene was carried out in the same way; analysis was performed on the silicone column (220°). A mixture

of durene (4.44 g) and mesitylene (4.09 g) was oxidised likewise, with lead tetra-acetate (2.1 g) in trifluoroacetic acid (18 g). It was not possible to obtain complete separation of the diarylmethanes (15) and (22) by column chromatography and fractional recrystallisation, but oxidation of a mixture of durene (4.0 g) and mesitylene (14.4 g) produced comparatively little of the former, and chromatography gave 2,4,5-trimethylphenyl-(2,4,6-trimethylphenyl)methane (22) as crystals, m.p. 97–98° (from ethanol) (Found: C, 90.5; H, 9.7. C₁₉H₂₄ requires C, 90.4; H, 9.6%); τ 3.09 (1H, s, ArH), 3.14 (2H, s, ArH), 3.76 (1H, s, ArH), 6.21 (2H, s, CH₂), 7.69 (3H, s, Me), 7.72 (3H, s, Me), 7.88 (9H, s, Me), and 7.99 (3H, s, Me).

Oxidation of a mixture of durene (6.81 g) and anisole (5.52 g), with lead tetra-acetate (4 g) in trifluoroacetic acid (28 g), was carried out as before. Work-up of the deep green solution after 24 h as in (a) and preparative g.l.c. gave 2,3,5,6-tetramethyl-4'-methoxybiphenyl (25) as crystals, m.p. 80.5–81.5° (from methanol) (Found: C, 85.1; H, 8.5. C₁₇H₂₀O requires C, 85.0; H, 8.4%); τ 3.17 (4H, s, ArH), 3.20 (1H, s, ArH), 6.28 (3H, s, OMe), 7.83 (6H, s, Me), and 8.18 (6H, s, Me).

A mixture of durene (6.26 g), anisole (5.05 g), and mesitylene (5.60 g) was oxidised in the same way; g.l.c. was performed on the silicone column (220°).

(e) *Hexamethylbenzene*. A mixture of hexamethylbenzene (1.62 g) and benzene (7.8 g) in dichloromethane (20 ml) was oxidised in the same way as for durene, with lead tetra-acetate (2.36 g) in trifluoroacetic acid (11 g). Work-up after 3 days followed by preparative g.l.c. gave benzylpentamethylbenzene (27) as crystals, m.p. 110–111° (from methanol) (Found: C, 90.6; H, 9.3. C₁₆H₂₂ requires C, 90.7; H, 9.3%); *m/e* 238 (M⁺, 100%), 223 (67, M – Me), and 160 (15, C₁₂H₁₈).

A mixture of hexamethylbenzene (3.25 g) and mesitylene (12.5 g) in dichloromethane (75 ml) was oxidised in the same way with lead tetra-acetate (2.9 g) in trifluoroacetic acid (18 g). Work-up of the deep red solution after 24 h and preparative g.l.c. gave pentamethylphenyl-(2,4,6-trimethylphenyl)methane (28) as crystals, m.p. 130–130.5° (from methanol) (Found: C, 89.9; H, 10.0. C₂₁H₂₃ requires C, 89.9; H, 10.1%); *m/e* 280 (M⁺, 39%), 265 (37, M – Me), 160 (90, C₁₂H₁₆), and 132 (100, C₁₀H₁₂).

In control experiments, aryl acetates were found not to be hydrolysed during work-up, and no oxidation products were found when a solution of mesitylene, durene, or hexamethylbenzene in dichloromethane and trifluoroacetic acid was analysed after several weeks.

We thank the S.R.C. for a studentship to J. S. W.

[2/1567 Received, 30th October, 1972]

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