Reactions of Palladium(II) with Organic Compounds. Part II.[1] Oxidation of Some Benzenoid Compounds in Trifluoroacetic Acid

By Ferrers R. S. Clark, Richard O. C. Norman,* C. Barry Thomas, and John S. Willson, Department of Chemistry, The University of York, Heslington, York YO1 5DD

Benzene, some monosubstituted benzenes, and di- and poly-methylated benzenes are readily oxidised by palladium-(II) in trifluoroacetic acid. Benzene and most monosubstituted analogues give mainly or solely biaryls, as do o-xylene, m-xylene, and hemimellitene (1,2,3-trimethylbenzene). Most of the possible isomers were found in each case but the predominant ones are those in which one of the aryl groups is bonded to the second through the position most susceptible to electrophilic attack. Toluene, ethylbenzene, p-xylene, and pseudocumene (1,2,4-tri-methylbenzene) give, in addition, diarylmethanes, and from mesitylene and durene (1,2,4,5-tetramethylbenzene) these latter compounds were the only products detected. Diarylmethane formation, in most cases, was of necessity selective but, even in those instances where more than one such compound might have been expected, only the anticipated product of electrophilic arylmethylation was observed. Mechanisms which account for the formation of the two types of product are discussed.

AROMATIC compounds have long been known to react with metal salts; halogenation, arylmethylation, nuclear coupling to form biaryls, and polymerisation have all been observed.[2,3] There have been several recent reports that palladium(II) salts bring about some of these, and related, reactions; the products most commonly found are those resulting from oxidative dimerisation, ring acetoxylation, and (for methyl-substituted aromatic hydrocarbons) side-chain acetoxylation. Thus, benzene gives biphenyl with either [4] palladium(II) chloride in the presence of sodium acetate in acetic acid at 90° or [5] palladium(II) acetate in acetic acid at 100°. In contrast, palladium(II) nitrate in acetic acid at ca. 100° yields mainly phenyl acetate,[6] and it has been found that ring-acetoxylation of other benzenoid compounds by palladium(II) nitrate is favoured, compared with alternative reactions, by avoiding an excess of acetate ion and working in an atmosphere of oxygen.[7] With toluene, side-chain acetoxylation can compete with oxidative dimerisation. For example, whereas palladium(II) chloride in hot acetic acid containing sodium acetate gives mainly the six bitolyls,[8] palladium(II) acetate in hot acetic acid containing potassium acetate gives more benzyl acetate than bitolyls;[9] the ratio of the amounts of the two types

of product increases with the ratio [KOAc] : [Pd(OAc)$_2$].[9] There are also indications that the efficiency of side-chain acetoxylation increases on the introduction of electron-releasing substituents into the aromatic ring.[10]

Maitlis has recently reviewed the oxidative dimerisations induced by palladium(II) and has concluded that electrophilic palladation, followed by a rapid, concerted coupling to give biaryl and palladium(I), best explains the available data.[11] He has also discussed both ring and side-chain acetoxylation; the active species in each case may be a palladium(I) complex.[12]

The above three types of reaction brought about by palladium(II) salts are also effected by lead(IV) salts under appropriate conditions. Moreover, the two oxidants are both, formally, two-electron acceptors. We have recently obtained mechanistic information about the reactions of benzene, monosubstituted benzenes, and some di- and poly-methylated derivatives with lead(IV) in trifluoroacetic acid;[13,14] we chose to study the reactions of such compounds with palladium(II) in trifluoroacetic acid in order to compare the characteristics of the two oxidants and in the hope of elucidating mechanistic features in the reactions of the latter.

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RESULTS AND DISCUSSION

Oxidation Products.—Oxidations were carried out with palladium(II) acetate in trifluoroacetic acid at room temperature; a large excess of the aromatic compound was used so as to minimise the occurrence of oxidation of products. Reaction mixtures were worked up by hydrolytic treatment when the deposition of palladium appeared to be complete (usually several days). Yields are based on palladium(II).

Benzene gave mainly biphenyl (30—40%, varying with the relative amounts of the reagents), with traces of terphenyl and phenol. When the reaction was carried out in the presence of a ten-fold excess of copper(II)

factors which determine the relative ease of formation of these two types of product.

The most significant evidence was derived by studying the variation in the yields of the two products with time. The yield of each product increased monotonically, but whereas the yield of the biaryl had essentially reached its final value after *ca.* 4 h, that of the diarylmethane reached its final value only after *ca.* 9 days and after 4 h its formation was only *ca.* 10% complete. The inference from this result is that the consumption of the initial palladium(II) occurs relatively rapidly but, whereas the biaryl is formed quickly, formation of the diarylmethane involves an

TABLE 1

Products (%) from the oxidation of monosubstituted benzenes with Pd(OAc)$_2$ in trifluoroacetic acid at room temperature

| Reactants | Biaryls | | | | | | XC$_6$H$_4$Ph | | | PhPh | Other | Total |
	2,2'	2,3'	2,4'	3,3'	3,4'	4,4'	2	3	4			
PhOMe	4	3.5	17		7	17						48.5
PhEt	1	3.5	11	4	17	16					6ᵃ	58.5
PhBuᵗ				5	20	17					4ᵇ	46
PhNO₂ᶜ		10	3	4	3	1						21
PhOMe + PhH	3	3	14		4	13	7	3	23	7		77
PhEt + PhH	1	1.5	4	2	8	8	1	3.5	9	2	3ᵃ	43
PhBuᵗ + PhH				4	12	10		7	12	3	2ᵇ	50
PhNO₂ + PhH ᵈ							25	42	13	20		

ᵃ *p*-EtC₆H₄·CHMePh.   ᵇ *p*-BuᵗC₆H₄·OH.   ᶜ Reflux temperature.   ᵈ 130-Fold excess of PhNO₂; yields relative only.

acetate, the yield of biphenyl was 113%, indicating reoxidation of reduced palladium, and that of the terphenyl was 10% (*o*-, 4; *m*-, 3.5; *p*-, 2%).

Anisole, ethylbenzene, and t-butylbenzene gave the corresponding disubstituted biaryls in yields recorded in Table 1; toluene gave bitolyls, but the isomers could not be resolved adequately by g.l.c. Toluene and ethylbenzene also gave small amounts of diarylmethanes [phenyl-*p*-tolylmethane and 1-(4-ethylphenyl)-1-phenylethane, respectively], and t-butylbenzene gave some 4-t-butylphenol. The yields of biaryls from nitrobenzene were very small after 7 days at room temperature, but significant after 2 days under reflux. Table 1 also gives results for the oxidations of mixtures of benzene and a monosubstituted benzene.

Both *o*- and *m*-xylene yielded biaryls. The former gave the three isomers (1)—(3) in relative amounts 22 : 10 : 1, and the latter gave the biaryl (4) as major product, and traces of two materials which, by their g.l.c. retention times, were probably isomeric biaryls (*cf.* ref. 14). In contrast, although *p*-xylene gave 19% of the biaryl (5), the major product was the diarylmethane (6) (38%). Pseudocumene likewise gave both a biaryl and diarylmethanes; the ratios of yields of compounds (7)—(10) were 12 : 8 : 1 : 1. Mesitylene gave 60% of the diarylmethane (11); neither bimesityl nor mesitol was detected. Hemimellitene gave three products which were shown by mass spectrometry to be biaryls.[14] Durene afforded the diarylmethane (12) in 60% yield.

Reactions of p-*Xylene.*—Since the oxidation of *p*-xylene gives comparable amounts of a biaryl and a diarylmethane, it was a suitable compound for a study of the

intermediate which yields the product slowly. If this inference is correct, then the addition of another benzenoid compound some time after the start of the
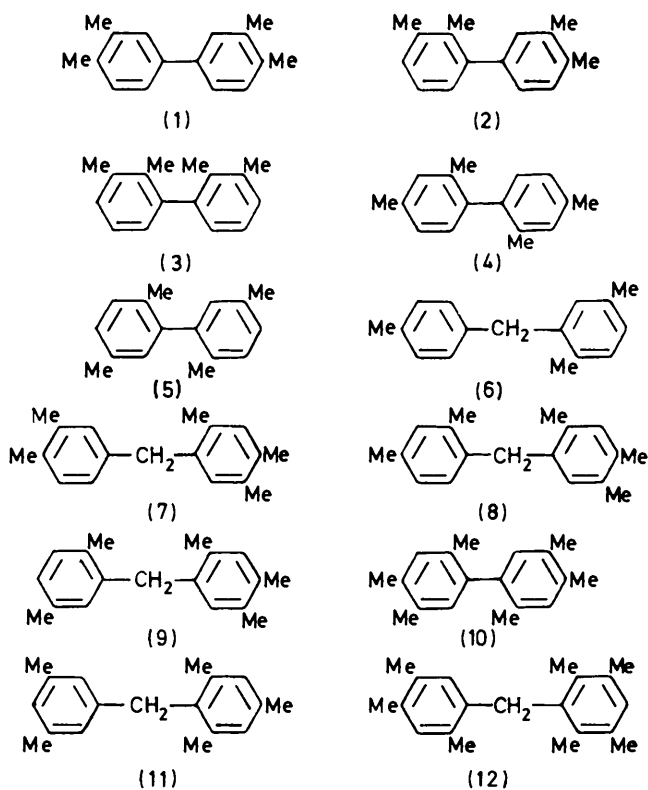
reaction but before its completion should give a different product distribution from that obtained when both

p-xylene and the second benzenoid compound are present from the start. We tested this hypothesis by employing a standard set of conditions for the oxidation of *p*-xylene [0·72 mmol Pd(OAc)$_2$, 40 ml *p*-xylene, 10 ml CF$_3$CO$_2$H] and adding mesitylene (10 ml) after given intervals; the products were those observed before for *p*-xylene, (5) and (6), and for mesitylene,

(13)

(14)

(15)
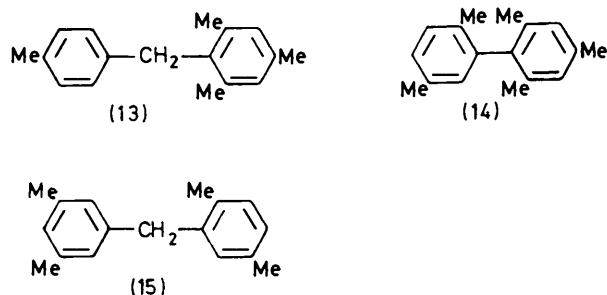
(11), together with three mixed products, (13)—(15). The results are in Table 2.

TABLE 2

Distribution of products (expressed as % of the total identified products) from the oxidation of *p*-xylene with the addition of mesitylene at various times after the start of the reaction

Time of addition	Products					
	(6)	(5)	(11)	(13)	(14)	(15)
3 min	1	11	67	13	1	7
18 min	8	34	30	26		2
4·5 h	13	35	23	28		1
24 h	33	41	11	15		Trace

We see that, if mesitylene is added early enough (3 min), the major product, (11), is one derived from mesitylene and an arylmethylating agent from mesitylene; comparatively little of the palladium(II) can have been used up in this time. However, when the addition of mesitylene is delayed even for only 18 min, the yield of (13), which is derived from mesitylene and an arylmethylating agent from *p*-xylene, is hardly less than that of (11) and, when addition is delayed longer, it is greater. Thus, the data are compatible with the view that a complex is formed from *p*-xylene and palladium(II) which has the capacity to aryl-methylate and which is destroyed much less rapidly than the initial palladium(II). Even when mesitylene is not added for 24 h, some of the complex is still available to form product (13).

The oxidation of an equimolar mixture of *p*-xylene with either chlorobenzene or nitrobenzene gave only those products which are formed from *p*-xylene alone. However, when benzene or anisole was the co-reactant, products derived from these compounds were also obtained (Table 3). The order of reactivity towards the arylmethylating agent from *p*-xylene which is shown by these results (anisole > *p*-xylene > benzene > chlorobenzene, nitrobenzene) indicates that the agent is electrophilic.

Reactions of Mesitylene.—When mesitylene was oxid-

ised with an equimolar amount of benzene, *p*-xylene, or anisole, only the diarylmethane (11) was obtained. However, with a ten-fold excess of benzene the products were (11), (16), (17), and biphenyl (18 : 2·5 : 1 : 3). Oxidation with an equimolar amount of durene gave 65% of the diarylmethane (18), as well as 4% of each of (11) and (12). It follows that durene is more readily

TABLE 3

Products of competition between *p*-xylene and other aromatic compounds [a]

	Normal *p*-xylene products		
ArH [b]	Biaryl	Diaryl-methane	Others
PhH	10	78	4-MeC$_6$H$_4$·CH$_2$Ph (1), 2,5-Me$_2$C$_6$H$_3$Ph (9), PhPh (2)
20PhH	Trace	20	4-MeC$_6$H$_4$·CH$_2$Ph (11), 2,5-Me$_2$C$_6$H$_3$Ph (11), PhPh (57)
PhOMe	7	30	2-Methoxy-4'-methyl-diphenylmethane (51), 4-Methoxy-4'-methyl-diphenylmethane (12)

[a] Figures are all relative yields. [b] Equimolar quantities of *p*-xylene and ArH were used except where noted.

converted into an arylmethylating agent than is mesitylene, and mesitylene is the more reactive of the two towards this entity.

(16)

(17)

(18)
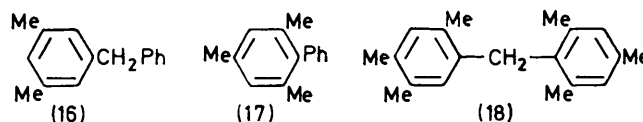
When a solution of mesitylene in trifluoroacetic acid ($\lambda_{max.}$ 265 nm; optical density 1·2) was added to one of palladium(II) acetate in trifluoroacetic acid ($\lambda_{max.}$ 263 nm; optical density 1·7), the optical density (1·8 at $\lambda_{max.}$ 266 nm) was greater than corresponds to a simple mixture (1·45), consistent with the formation of a complex. The optical density at 266 nm increased steadily for 3 h, during which time a small, broad peak at 390 nm increased and moved to 364 nm; after *ca.* 4 h, both peaks began to decrease and small, sharp peaks appeared at 326 and 356 nm which were not due to bimesityl or the diarylmethane (11). These changes were complete after 24 h and there was no further variation during 5 days.

Possible Reaction Mechanisms.—Comparison with oxidations by lead(IV) in trifluoroacetic acid. Under our conditions, the following aromatic compounds give mainly or entirely biaryls: benzene, anisole, toluene, ethylbenzene, t-butylbenzene, nitrobenzene, *o*- and *m*-xylene, and hemimellitene; the following yield mainly or solely diarylmethanes: mesitylene, pseudo-cumene, and durene; and *p*-xylene occupies an intermediate position. There are obvious general similarities to the behaviour of lead tetra-acetate in trifluoroacetic acid, but there are also three

notable differences.[13,14] First, the lead(IV) oxidant yields, from benzene, more phenol (via phenyl trifluoroacetate) than biphenyl and likewise, from toluene, more cresols than bitolyls. Secondly, the isomeric distribution of the dimethoxybiphenyls from anisole differs markedly for the two oxidants for example, with lead(IV) the 2,3'-isomer is not detectable and the 3,4'-isomer is formed in only trace amounts, the reaction with palladium(II) being much less selective. Thirdly, with lead(IV) neither mesitylene nor pseudocumene affords an arylmethylating agent effectively; the former yields 65% of bimesityl and only a trace of the diarylmethane (11) and the latter yields mainly the biaryl (10) and only traces of the diarylmethanes such as (7).

The first difference argues against the mediation of aryl cations during oxidation with palladium(II); certainly phenyl and tolyl cations, if formed from benzene and toluene, would be expected to yield trifluoroacetate esters through attack by solvent. The other two differences argue against the mediation of aromatic radical cations in the palladium(II) reactions; for example, the bimesityl formed from mesitylene and lead(IV) in otherwise similar conditions is considered to arise via trapping of the mesitylene radical cation by mesitylene (cf. its formation by the anodic oxidation of mesitylene [15]).

Biaryl formation. Palladation followed by concerted coupling of two arylpalladium species [11] does not satisfactorily account for biaryl formation under our conditions. For example, in the competitive reaction of t-butylbenzene and benzene (Table 1) the ratios of yields of $(Bu^tC_6H_4)_2$, $Bu^tC_6H_4Ph$, and Ph_2 are 9 : 6 : 1. If the cross-coupled product can only be formed by concerted reaction of PhPdX and $Bu^tC_6H_4PdX$ then the low yield of biphenyl cannot be explained. Similarly, the absence of dinitrobiphenyls in the competitive reaction of nitrobenzene and benzene is inconsistent with this hypothesis, as are the isomer distributions obtained from monosubstituted arenes alone.

The proportions of the products outlined in Table 1, however, suggest that one of the two aromatic nuclei reacts preferentially at the position(s) which is the most reactive towards electrophilic reagents, whereas the other nucleus reacts in a less discriminating manner. For example, ca. 80% of the dinitrobiphenyls is accounted for by isomers substituted at the 3-position in at least one ring but only ca. 20% is the 3,3'-isomer. Similarly, nearly 90% of the di-t-butylbiphenyls have been formed by reaction through the 4-position in at least one ring, but only 40% is the 4,4'-isomer. Again, there is little selectivity in the formation of the three nitrobiphenyls from benzene and nitrobenzene but significant selectivity in that of the methoxybiphenyls from benzene and anisole, possibly because nitrobenzene

is the non-discriminating component in the former case but benzene is in the latter.

These differing selectivities can be accommodated by a modification (Scheme 1) of the mechanism recently put forward to account for the oxidation of benzenoid compounds by palladium(II) in acetic acid.[16] In essence palladation of an arene occurs to form RC_6H_4 PdX (referred to as $ArPd^+$ by Eberson [16]) which adds to the aromatic ring; loss of HPdX then leads to the observed products. It is probable, from a comparison with the earlier work,[16] that it is in the first step that the greater selectivity occurs. It is worth noting too that this mechanism can be adapted to embrace the results of palladium-induced arylation of olefins.[17]
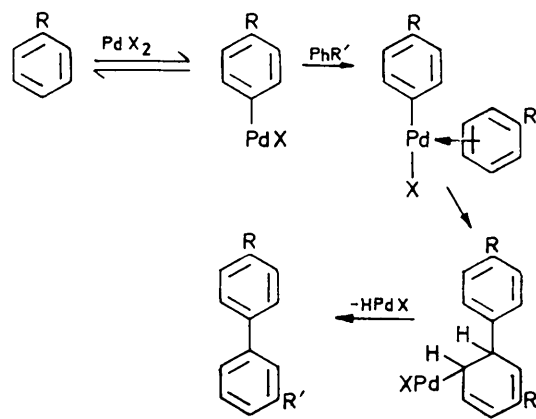
SCHEME 1

The one remaining anomaly is that p-xylene oxidatively dimerises much more readily than does anisole in a competitive reaction (Table 3). This is the reverse of the order found in S_E2 reactions [18] but it has been observed previously that the electron-donating ability of aryl-bonded methoxy is significantly reduced when trifluoroacetic acid is employed as solvent.[19]

Diarylmethane formation. We found, from oxidation of a mixture of mesitylene and benzene, that the arylmethylating agent from the former attacks mesitylene some 70 times faster than it does benzene and, from oxidation of mesitylene and durene, that the arylmethylating agent from durene attacks mesitylene about 16 times faster than it attacks durene. In addition, whereas pseudocumene gives all three possible arylmethylating agents, each attacks, almost exclusively, the 5-position of another substrate molecule. These selectivities are much greater than would be expected for substitution by an arylmethyl radical but are fully consistent with reaction of a benzylic cation or incipient benzylic cation. We are not able to elucidate the mode of generation of this species but note that the only instances of high yields of diarylmethanes are those in which the vacant sites on the aromatic ring are adjacent to methyl substituents. We tentatively

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suggest therefore that the reactive entity is a π-allyl complex, e.g. (19),[20] generated either via palladation of an unsubstituted position in the aromatic ring and loss of a proton from the side chain, or by concerted rearrangement of a π-complex in which the palladium is co-ordinated to a 'localised' double bond [21] rather than the aromatic ring as a whole (Scheme 2).
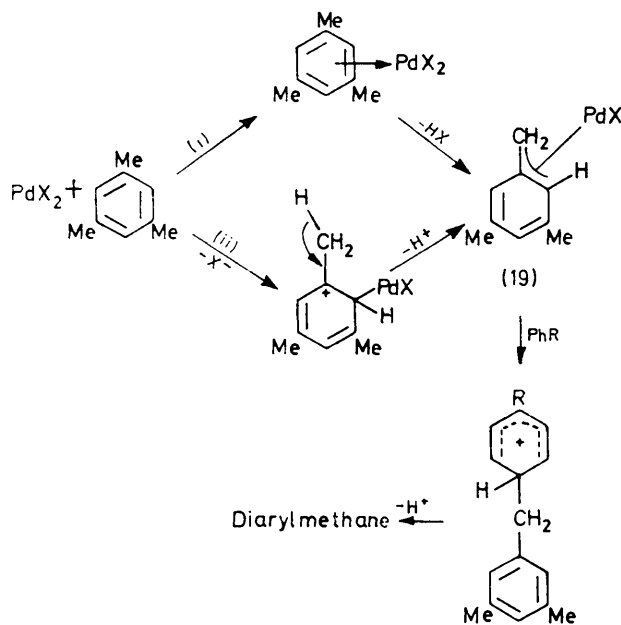
SCHEME 2

EXPERIMENTAL

The analytical methods [13] and many of the materials used [13,14] have been described. The stationary phases for g.l.c. were usually acid-washed diethylene glycol adipate (DEGA) and silicone oil SE 30; preparative g.l.c. was performed on a Pye instrument (series 105).

Reference Compounds.—4-t-Butylbiphenyl and 4,4'-di-t-butylbiphenyl were prepared from biphenyl and t-butyl alcohol in the presence of aluminium trichloride,[22] separated by fractional distillation, and obtained as solids, m.p. 51—52° (from ethanol) (lit.,[23] 51·5—52·5°) and 126—127° (from ethanol) (lit.,[23] 127—128°), respectively; preparative g.l.c. of the fraction of b.p. ca. 120° at 0·7 mmHg gave 3-t-butylbiphenyl (lit.,[24] 105° at 0·4 mmHg), $\lambda_{max.}$ (MeOH) 250 nm (log ε/m^2 mol^{-1} 3·20), τ (CCl$_4$) 2·40—2·80 (9H, m, ArH) and 8·64 (9H, s, Me).

Acetylation of biphenyl and subsequent Clemmensen reduction gave a mixture of 2- and 4-ethylbiphenyl containing 90% of the 4-isomer (m.p. 26°; lit.,[25] 46—47°); τ (CCl$_4$) 2·40—3·0 (9H, m, ArH), 7·45 (2H, q, J 8 Hz, benzylic CH$_2$), and 8·80 (3H, t, J 8 Hz, Me); acetylation gave 4-acetyl-4'-ethylbiphenyl, which was reduced by the Clemmensen method to give 4,4'-diethylbiphenyl (m.p. 76—78°; lit.,[25] 81°); τ (CCl$_4$) 2·80 (8H, 2d, J 10 Hz, ArH), 7·40 (4H, q, J 7 Hz, CH$_2$), and 8·78 (6H, t, J 7 Hz,

Me). The nitro- and dinitro-biphenyls were available in this laboratory.[26]

Oxidations.—For the oxidation of benzene, the following procedure was typical. Trifluoroacetic acid (16·5 g) was added to a suspension of palladium(II) acetate (0·114 g) in benzene (1·56 g) at room temperature. After 24 h the solution and precipitated palladium were poured into water (200 ml) and an ethereal extract was shaken with M-NaOH. After acidification (2M-HCl), the solution was neutralised (NaHCO$_3$), and the ethereal solution and ethereal extract of the aqueous solution were combined, dried (MgSO$_4$), and evaporated to ca. 50 ml. The product was analysed by g.l.c. and mass spectrometry; quantitative analysis for biphenyl and phenol was carried out on the DEGA column (180°) with bibenzyl as internal standard. A reaction was also carried out with trifluoroacetic acid (11·5 g), palladium(II) acetate (0·113 g), copper(II) acetate monohydrate (1·0 g), and benzene (3·88 g) for 4 days in an atmosphere of nitrogen; quantitative determination of biphenyl and the terphenyls was carried out on the silicone column (220°) with bibenzyl as internal standard.

Anisole and toluene were oxidised as in the first method for benzene; reactions were worked up after 14 days and quantitative analysis was carried out on the silicone column (200°) with biphenyl as internal standard.

Ethylbenzene was oxidised by the addition of trifluoroacetic acid (15 g) to a suspension of palladium(II) acetate (0·214 g) in ethylbenzene (6·75 g) at room temperature. The mixture was worked up after 14 days; quantitative analysis was carried out on the silicone column (200°) [27] with phenanthrene as internal standard. t-Butylbenzene was oxidised likewise; quantitative determination of p-t-butylphenol and the di-t-butylbiphenyls was performed on the DEGA column (190°) with phenanthrene as internal standard. Removal of phenolic products by washing the ethereal solution with sodium hydroxide followed by preparative g.l.c. gave 3,3'-di-t-butylbiphenyl (Found: M^+ 266·2038. $C_{20}H_{26}$ requires M, 266·2035); $\lambda_{max.}$ 250 nm (log ε/m^2 mol^{-1} 3·25); τ (CCl$_4$) 2·45—2·80 (8H, m, ArH) and 8·61 (18H, s, Me); and 3,4'-di-t-butylbiphenyl (Found: M^+ 266·2031); $\lambda_{max.}$ 254 nm (log ε/m^2 mol^{-1} 3·31); τ (CCl$_4$) 2·45—2·80 (8H, m, ArH) and 8·65 (18H, s, Me).

Nitrobenzene was oxidised, typically, by heating a solution of palladium(II) acetate (0·226 g) and nitrobenzene (1·26 g) in trifluoroacetic acid (22·5 g) under reflux for 2 days; quantitative analysis was performed on the silicone column (200°).

For the oxidation of the xylenes, a typical procedure was as follows. Trifluoroacetic acid (34·3 g) was added to a suspension of palladium(II) acetate (0·227 g) in p-xylene (5·31 g) at room temperature and the mixture was set aside for 14 days; quantitative analysis was carried out on the silicone column (200°) with biphenyl as internal standard. Preparative g.l.c. of the combined products of several reactions gave 2,4',5-trimethyldiphenylmethane [τ (CCl$_4$) 2·95—3·35 (7H, m, ArH), 6·21 (2H, s, CH$_2$), 7·76 (6H, s, Me), and 7·88 (3H, s, Me)] and 2,2',5,5'-tetramethylbiphenyl [τ (CCl$_4$) 3·00—3·30 (6H, m, ArH), 7·73 (6H, s, Me), and

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[26] C. B. Thomas and J. S. Willson, J.C.S. Perkin II, 1972, 779.
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8·04 (6H, s, Me)]. Mesitylene was oxidised likewise; in one reaction, copper(II) acetate monohydrate was included and the mixture was worked up after 4 days to give 2,3′,4,5′,6-pentamethyldiphenylmethane, m.p. 65—66° [from ethanol (charcoal)] (lit.,[28] 67°); τ 3·05—3·45 (5H, m, ArH), 6·09 (2H, s, CH_2), 7·74 (3H, s, Me), and 7·81 (12H, s, Me). Reactions involving pseudocumene, hemimellitene, and durene were carried out in the same way; quantitative analysis was performed on the silicone column (220°) with either biphenyl or 4-t-butylbiphenyl as internal standard.

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