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Homolytic Aromatic Substitution. Part XXXIV.† Major Products from the Reaction of Benzoyl Peroxide with *p*-Disubstituted Benzenes

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The reaction of benzoyl peroxide with *para*-disubstituted benzenes (excluding those with sulphur-containing substituents) can lead to substitution by phenyl and/or benzoyloxy-radicals. Product formation is dependent upon the nature of the substituent groups and may be correlated with Hammett σ_p values. In *para*-substituted toluenes, the formation of bibenzyls is reduced with increase in the σ_p value of the *para*-substituent. Neither phenylation nor benzoyloxylation of the aromatic ring is observed in the reactions of benzoyl peroxide with methyl phenyl sulphide, methyl *p*-tolyl sulphide, or methyl *p*-tolyl sulphoxide. The major reaction is oxidation at the sulphur atom, which leads to the formation of, in addition to benzoic anhydride, arylthiomethyl and arylsulphinylmethyl benzoates from the aryl sulphides and sulphoxides respectively. There is no evidence that free radicals are involved in the reaction of benzoyl peroxide with these sulphur-containing compounds.

THE reactions of benzoyl peroxide with some *para*-disubstituted benzenes have been examined in order to obtain further information on the effect of substituent groups in an aromatic ring in determining the position and ease of substitution by phenyl radicals.¹ Since the substituent groups can be chosen to be of similar or of opposite electronic properties, this reaction should provide information on the importance of the electronic effects of groups in affecting the substitution reaction.

[†] Part XXXIII, D. H. Hey, M. J. Perkins, and G. H. Williams, J. Chem. Soc., 1965, 110. *para*-Disubstituted benzenes have the advantage that even when the substituents are different, only two products of monophenylation can be formed.

In these reactions difficulties in the work-up arise due to the need to remove excess of high-boiling, and often solid, *para*-disubstituted benzenes. A concentration of benzoyl peroxide in *para*-disubstituted benzene of 5 g in 100 g was used in most of the reactions designed to isolate and identify the major biaryl-type products.

¹ Part II, D. R. Augood, D. H. Hey, and G. H. Williams, J. Chem. Soc., 1952, 2094, and subsequent papers in this series.

J. Chem. Soc. (C), 1970

Table 1 records the products of the reaction of benzoyl peroxide with some symmetrically para-disubstituted benzenes (I).



Previous workers have shown that the decomposition of benzoyl peroxide in p-dichlorobenzene (Ia)^{2,3} and in p-di-t-butylbenzene (Ic)⁴ affords, respectively, 2,5-dichlorobiphenyl (IIa) and 2,5-di-t-butylbiphenyl (IIc) as

TABLE 1

Products of the reaction of benzoyl peroxide (5 g) with symmetrically p-disubstituted benzenes (I) (100 g)

¢-Disub-					Column
stituted		Benzoic	Biaryl	Benzoate	for g.l.c.
benzene	X	acid/g *	(II)/g *	(III)/g *	analysis †
(Ia)	C1	1.65	1.91	Trace	С
		(0.6555)	(0.828)		
(Ib)	\mathbf{Br}	2.505	3.045	Trace	в
• •		(0.993)	(0.471)		
(Ic)	$\mathbf{Bu^t}$	1.60	1.310	Trace?	в
		(0.635)	(0.238)		
(Id)	OMe	3.455	. ,	$2 \cdot 130$	в
, /		(1.362)		(0.390)	

* Yield in parentheses in mole per mole of Bz_2O_2 . † All analyses were carried out at 200° with bibenzyl as marker except in the case of p-dimethoxybenzene (Id), when 4-bromobiphenyl was used as marker.

major products; we have obtained similar results with more concentrated solutions. p-Dibromobenzene (Ib) similarly gives 2,5-dibromobiphenyl (IIb). Esters of

they can decompose to give phenyl radicals. Alternatively, benzoyl peroxide may react with p-dimethoxybenzene (Id) by the route outlined in Scheme 1, involving initial attack on the methoxy-group in the manner proposed by Lynch and Moore,⁵ to accommodate preferential *ortho*-benzoyloxylation of anisole. This is analogous to the scheme of Walling and Hodgdon ⁶ for the benzoyloxylation of phenols by benzoyl peroxide, which is accelerated by the presence of electron-donating groups. Ester formation in the reaction of benzoyl peroxide with anisole is much greater than with other monosubstituted benzenes, and the presence of the second methoxy-group in p-dimethoxybenzene (Id) enhances ester formation so that it predominates over phenylation.

$$(Id) + PhCO_{2} \longrightarrow [p-MeO \cdot C_{6}H_{4} \cdot \dot{O}Me]^{\dagger} + PhCO_{2}^{-}$$

$$(IV)$$



The reaction of benzoyl peroxide with p-xylene (Va) was shown by Augood 7(a) to afford 2,5-dimethylbiphenyl (VIa) and 4,4'-dimethylbibenzyl (VIIIa) as major products. This result is now confirmed under the

Method of Ratio (%) p-Substituted Benzoic Biaryls ratio Column for » х acid/g * (VI + VII)/g *(VI) (VII) determination Bibenzyl/g * g.l.c. analysis toluene 1.70 0.8130.985(Va) • Me в (0.675)(0.216)(0.226)(Vb) Cl 1.76050.050.0С 1.24N.m.r. 0.199(0.493)(0.419)52.048.0G.l.c. (0.038)(Vc) \mathbf{Br} 1.510 45.254.8N.m.r. С 2.44Trace (0.295)(0.963)(Vd) NO, 76.133.9 в 2.1451.345N.m.r. 27.0(0.849)(0.303)73.0G.1.c. (Ve) CO₂Me 1.0251.28553.446.6N.m.r. С (0.406)(0.275)53.6G.1.c. 46.4* Yield in mole per mole of Bz₂O₂ given in parentheses.

^a Also formed: (IX) (0.118 g), (X) (0.0173 g). ^b All analyses carried out at 200° with bibenzyl as marker.

type (III) are, at best, trace products in these reactions, but, in contrast, p-dimethoxybenzene (Id) has been reported to afford 2,5-dimethoxyphenyl benzoate (IIId) as a major product,⁵ a result which is now confirmed. These results suggest that p-dimethoxybenzene (Id) is so reactive that it removes benzoyloxy-radicals before

 Part III, D. R. Augood, D. H. Hey, and G. H. Williams, J. Chem. Soc., 1953, 44.
 M. Karelsky and K. H. Pausacker, Austral. J. Chem., 1958,

⁸ M. Karelsky and K. H. Pausacker, Austral. J. Chem., 1958, 11, 39.

⁴ Part VII, J. I. G. Cadogan, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 1954, 3352. present conditions, but, like Foster and Williams,^{7(b)} we also found that 2,5-dimethylphenyl benzoate (IX) and 4-methylbenzyl benzoate (X) are formed as minor products. This reaction has now been extended to the *para*-substituted toluenes (Vb—e). The major products (Table 2) are the biaryls of types (VI) and (VII), and the 5 B. M. Lynch and R. B. Moore, *Canad. J. Chem.*, 1962, **40**,

1461. ⁶ C. Walling and R. B. Hodgdon, jun., J. Amer. Chem. Soc., 1958, **80**, 228.

1958, **80**, 228. ⁷ (a) D. R. Augood, Ph.D. Thesis, London, 1952; (b) W. R. Foster and G. H. Williams, J. Chem. Soc., 1962, 2862.

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TABLE 2

Products of the reaction of benzoyl peroxide (5 g) with p-substituted toluenes (V) (100 g)

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bibenzyls (VIII). The amount of substituted bibenzyl (VIII) formed is reduced as the electrophilic character of the substituent X in the substituted toluene (V) is increased, *i.e.* the yield of (VIII) decreases in the order



 $X = Me > Cl > Br > CO_2Me = NO_2$. This suggests that increasing the electrophilic character of the substituent X in (V) makes hydrogen atom abstraction from the methyl group more difficult compared to phenylation of the aromatic ring, *i.e.* electron-attracting groups cause the hydrogens of the methyl group to be bound more firmly to the carbon atom. In the case of p-nitrotoluene (Vd) the absence of 4,4'-dinitrobibenzyl (VIIId) may also be due to the removal of any p-nitrobenzyl radicals by reaction with nitro-groups, since Jackson and Waters⁸ have shown that benzyl radicals react readily with nitro-groups. The result recalls the earlier observations of Hambling, Hey, and Williams,9 who found that in the reaction of para-substituted benzoyl peroxides with toluene, bibenzyl formation was reduced as the electrophilic character of the substituent in the peroxide was increased. The ratio of the isomeric biaryls, (VI) and (VII), formed in the reaction of benzoyl peroxide with the unsymmetrical para-substituted toluenes (V) is also given in Table 2. With the exception of p-bromotoluene (Vc), in which steric effects are likely to be maximal, increasing the electrophilic character of the substituent X increases phenyl radical substitution ortho to the substituent X rather than to the methyl group. The phenylation of p-bromotoluene (Vc) may additionally involve an atypical pathway, since Gill and Williams 10 have shown that the phenylation of the related bromobenzene takes an unusual course. The partial rate factors F_{θ} for the phenylation of toluene,¹¹ chlorobenzene,¹¹ bromobenzene,¹¹ methyl benzoate,¹² and nitrobenzene,¹¹ are respectively 2.5, 1.6, 1.9, 3.0, and 5.5. To relate these values adequately to the observed results, F_o for chlorobenzene and bromobenzene should be more comparable to the value for toluene. The higher F_{o} values for methyl benzoate and nitrobenzene correlate well with the preference for phenylation ortho to the

methoxy carbonyl and nitro-groups respectively in (Ve) and (Vd).

The mixtures of biaryls (VI) and (VII) obtained in reactions with *para*-substituted toluenes (V) were analysed by a combination of n.m.r. and g.l.c. methods. G.l.c. analysis gave the proportions of the two isomers, and when authentic specimens were not available for comparative retention time studies, n.m.r. observations were used to correlate the product ratio with respect to specific isomers, on the assumption that the CH_3 signal in (VII) occurs at higher field than it does in (VI). This is based on the observation that the n.m.r. spectrum of 2,5-dimethylbiphenyl (VIIa) shows CH_3 signals at τ 7.71 (s) and 7.84 (s), which are assigned to the 5- and 2-methyl group protons respectively, on the assumption that the phenyl group shields a methyl group in the ortho-position more than one in the meta-position. This is supported by the observation that in 2- and 3-methylbiphenyl, the CH_3 signals occur, respectively, at τ 7.82 (s) and 7.70 (s).



The reaction of benzoyl peroxide with p-methoxytoluene (XI) afforded neither bibenzyl- nor biaryl-type products, and the major product was 2-methoxy-5-methylphenyl benzoate (XII). Thus the electronic effects of the methyl and methoxy-groups apparently combined to produce the same effect as two methoxygroups in p-dimethoxybenzene (Id), and lead to predominant benzoyloxylation.

The yields and proportions of the two biaryls (XIV) and (XV) formed in the reaction of benzoyl peroxide with p-chloronitrobenzene (XIIIa), p-nitroanisole (XIIIb), and methyl p-methoxybenzoate (XIIIc) are shown in Table 3. In each case there is a preference for substitution ortho to the more electrophilic substituent. A quantitative measure of the electronic character of the



 α ; X = Cl, Y = NO₂ b; X = NO₂, Y = OMe c; X = OMe, Y = CO₂Me

groups considered in compounds (V) and (XIII) can be obtained from Hammett σ values for these groups in the *para*-position: 13

Group OMe Me Cl \mathbf{Br} CO₂Me NO, Hammett -0.268 - 0.170 + 0.226 + 0.2322 +0.778 σ_p value

No figure is available for CO₂Me, but it is unlikely to

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⁸ R. A. Jackson and W. A. Waters, J. Chem. Soc., 1960,

^{1653.} ⁹ Part XXVII, J. K. Hambling, D. H. Hey, and G. H. Williams, J. Chem. Soc., 1962, 487.

differ substantially from the value of +0.522 quoted ¹³ for CO₂Et. All the results now reported, as summarised in Tables 1-3, show that substitution by the phenyl radical occurs preferentially at the position ortho to the substituent with the largest numerical σ_p value. Appreciable benzoyloxylation occurs only when both *para*-substituents have negative σ_p values. In *p*-nitroanisole (XIIIb) the positive σ_p value for the nitro-group is much greater than the negative σ_p value for the methoxy-group and hence phenylation predominates. A similar effect occurs with methyl p-methoxybenzoate (XIIIc), where the positive value of σ_p for the methoxy now been obtained for the reaction in the absence of chloroform. The methyl phenyl sulphoxide (XVIIa)



and benzoic anhydride most probably originate from nucleophilic attack by sulphur at the peroxidic oxygen atom to form an ion pair, which then rapidly reacts to

TABLE 3

Products of the reaction of benzoyl peroxide (5 g) with unsymmetrical p-disubstituted benzenes (XIII) (100 g)

b-Disubstituted			Benzoic	Biarvls	Ratio (%)		Method of ratio	Column + for
benzene	\mathbf{X}	Y	acid/g *	(XIV + XV)/g *	(XIV)	(XV)	determination	g.l.c. analysis
(XIIIa)	Cl	NO_2	1.644	3.355	69	31	G.l.c.	A
(XIIIb)	NO_2	OMe	$(0.651) \\ 2.600$	(0.683) 1.438	38	62	G.l.c.	А
(XIIIc)	ОМе	CO₂Me	(1.029) 2.400 (0.040)	(0.304) 1.375 (0.276)	66	34	G.l.c., n.m.r.	А

* Yield in mole per mole of Bz_2O_2 given in parentheses. \dagger 4-Bromobiphenyl used as marker in each case.

carbonyl group is likely to be numerically greater than the negative σ_p value of the methoxy-group.

In the reaction of benzoyl peroxide with p-chloronitrobenzene (XIIIa), g.l.c. analysis of the biaryl product indicated the presence of two isomers, with one predominating. The two isomers were differentiated by comparison with synthetic 2-chloro-5-nitrobiphenyl (XVa), which proved to be the minor component. Similarly an authentic specimen of 2-methoxy-5-nitrobiphenyl (XIVb) helped to distinguish the two products of the reaction of p-nitroanisole (XIIIb). The biaryl mixture [(XIVc) and (XVc)] from the reaction of benzoyl peroxide with methyl *p*-methoxybenzoate (XIIIc), could not be isolated in a pure state by preparative g.l.c. and was always contaminated with (XIIIc). The n.m.r. spectrum of this product exhibited five peaks in the τ 6.0—6.5 region in which OCH₃ and CO₂CH₃ proton resonances are expected. Apart from the single peak assigned to OCH_3 and CO_2CH_3 in (XIIIc) the strongest resonance was at τ 6.46 (s), and this was assigned to CO_2CH_3 in (XIVc), which is therefore the major isomer. This assignment was made by analogy with the observation that in the two biaryl products (VIe) and (VIIe) from the reaction of benzoyl peroxide with methyl p-toluate (Ve), the CO₂CH₃ signals are found in the n.m.r. spectrum at 6.48 (s) and 6.15 (s) respectively.

The decomposition of benzoyl peroxide in solutions of methyl phenyl sulphide (XVIa) in chloroform was studied by Horner and Jürgens.14 The products formed were, in addition to benzoic acid, methyl phenyl sulphoxide (XVIIa), benzoic anhydride, and phenylthiomethyl benzoate (XVIIIa). Similar results have afford these two products (Scheme 2). An alternative Scheme (3) in which the benzoate anion acts as a base towards hydrogen rather than as a nucleophile towards



PhCO·O·COPh + PhSOMe (XVIIa) SCHEME 2

carbon may accommodate the formation of phenylthiomethyl benzoate (XVIIIa). The intramolecular de-



composition indicated in Scheme 4 is a further possibility. The absence of 1,2-di(phenylthio)ethane as a product suggests that the PhS·CH₂· radical is not formed by hydrogen abstraction from phenyl methyl sulphide



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L. Horner and E. Jürgens, Annalen, 1957, 602, 135.
 H. B. Henbest, J. A. W. Reid, and C. J. M. Stirling, J. Chem. Soc., 1964, 1220.

(XVIa), and that the formation of phenylthiomethyl benzoate (XVIIIa) by the following induced-decomposition reaction with the peroxide is most unlikely.

$$\begin{array}{c} \operatorname{PhS} \cdot \operatorname{CH}_{2} \cdot + (\operatorname{PhCO}_{2})_{2} \longrightarrow \\ \operatorname{PhS} \cdot \operatorname{CH}_{2} \cdot \operatorname{O} \cdot \operatorname{COPh} (\operatorname{XVIIIa}) + \operatorname{PhCO}_{2} \cdot \end{array}$$

Henbest, Reid, and Stirling,¹⁵ who studied the reaction of phenyl methyl sulphide with di-t-butyl peroxide, found that dimerisation was a ready reaction of phenylthiomethyl radicals, and the absence of dimer in the reaction of benzoyl peroxide with methyl phenyl sulphide (XVIa) is therefore evidence that phenylthiomethyl radicals do not take part in that reaction.

The reaction of benzoyl peroxide with methyl p-tolyl sulphide (XVIb) is analogous to the reaction with methyl phenyl sulphide (XVIa), and affords methyl p-tolyl sulphoxide (XVIIb), benzoic anhydride, and p-tolylthiomethyl benzoate (XVIIIb). Again there was no evidence for free radical participation in this reaction. None of the dimer, $(p-MeS \cdot C_6 H_4 \cdot CH_2)_2$, formed in the reaction of di-t-butyl peroxide with methyl p-tolyl sulphide (XVIb),¹⁵ was found, which suggests that the p-thiomethylbenzyl radical p-MeS·C₆H₄·CH₂· does not participate in the reaction of benzoyl peroxide with methyl p-tolyl sulphide (XVIb). Benzoyl peroxide reacts with



methyl p-tolyl sulphoxide (XVIIb) to afford methyl p-tolyl sulphone (XIX), benzoic anhydride, and p-tolylsulphinylmethyl benzoate (XX). The reaction is therefore similar to those of the sulphides (XVIa) and (XVIb). The nucleophilic character of sulphur in the compounds (XVIa), (XVIb), and (XVIIb) results in exclusive reaction with the sulphur-containing groups in preference to thermal decomposition of benzoyl peroxide to give phenyl radicals which could substitute into the aromatic ring.

EXPERIMENTAL

N.m.r. spectra were determined with a Perkin-Elmer R10 spectrometer operating at 60 MHz, and i.r. spectra with a Perkin-Elmer 257 spectrometer.

By the literature method,¹⁶ in which a known quantity of marker is added to a solution for analysis, the yields of products recorded in Tables 1-3 were estimated by quantitative g.l.c. analysis with a Griffin D6 Density Balance Chromatograph and the following 6 ft $\times \frac{1}{4}$ in columns: A, 10% Apiezon L grease on Chromosorb W; B, 10% silicone oil on Chromosorb W; C, 10% polyethylene glycol 20M on Chromosorb W.

Preparative g.l.c. separations were carried out with a ¹⁶ C. S. G. Phillips and P. L. Timms, J. Chromatog., 1961, 5,

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- 18 G. Leandri, A. Mangini, and R. Passerini, J. Chem. Soc., 1957, 1386.
- ¹⁹ Th. Zincke and W. Frohneberg, Ber., 1910, 43, 848.

Varian Aerograph Autoprep A-705 and the following columns: D, 5 ft \times $\frac{3}{8}$ in of 30% silicone oil SE 30 on Chromosorb W; E, 20 ft $\times \frac{3}{5}$ in of 20% polyethylene glycol 20M on Chromosorb W. The mesh size for Chromosorb W was 60-80. Light petroleum had b.p. 60-80°.

The p-disubstituted benzene solvents, p-dichlorobenzene (Ia), m.p. 53°, p-dibromobenzene (Ib), m.p. 87°, p-dimethoxybenzene (Id), m.p. 56°, p-xylene (Va), b.p. 138°, pchlorotoluene (Vb), b.p. 162°, p-bromotoluene (Vc), b.p. 184°, p-nitrotoluene (Vd), m.p. 54°, p-chloronitrobenzene (XIIIa), m.p. 83°, and p-nitroanisole (XIIIb), m.p. 54°, were commercial samples purified by distillation or recrystallisation prior to use.

The following compounds were prepared by established procedures: p-methoxytoluene (XI), b.p. 175° (lit.,¹⁷ 175-176°), by methylation of p-cresol with methyl iodide in sodium hydroxide solution; p-di-t-butylbenzene (Ic),4 m.p. 77° (lit.,⁴ 76-77°); methyl p-toluate (Ve), m.p. 33° (lit.,¹⁷ $33\cdot2^{\circ}$), by esterification of *p*-toluic acid with methanol; methyl p-methoxybenzoate (XIIIc), m.p. 48° (lit., 17 48°), by esterification of p-methoxybenzoic acid with methanol; methyl phenyl sulphide (XVIa), b.p. 194-197° (lit.,17 194-196°), from the sodium salt of benzenethiol and methyl iodide; methyl p-tolyl sulphide (XVIb), b.p. 105° at 20 mmHg (lit.,¹⁷ 209° at 247 mmHg), from the sodium salt of p-thiocresol and methyl iodide; methyl phenyl sulphoxide (XVIIa),¹⁸ m.p. 31° (lit.,¹⁸ 31°); methyl p-tolyl sulphoxide (XVIIb),¹⁸ m.p. 51° (lit.,¹⁷ 50-54°); methyl p-tolyl sulphone (XIX),¹⁹ m.p. 89° (lit.,¹⁹ 89°); 4,4'-dimethylbibenzyl (VIIIa), m.p. 83° (lit.,¹⁷ 85°) from *p*-xylene and di-t-butyl peroxide; ²⁰ 4,4'-dichlorobibenzyl (VIIIb),²⁰ m.p. 102° (lit.,²⁰ 101°); 4,4'-dibromobibenzyl (VIIIc),²⁰ m.p. 114° (lit.,²⁰ 115°); 4,4'-dinitrobibenzyl (VIIId),²¹ m.p. 180° (lit.,²¹ 181°); 1,2-di(phenylthio)ethane, m.p. 69° (lit.,²² 69°), from ethylene dibromide and benzenethiol by a modification of the literature method,²² in which sodium ethoxide was the base in place of sodium hydroxide; 2,5-dimethylphenyl benzoate (IX), m.p. 61° (lit.,²³ 61°), from the triethylaminecatalysed reaction of p-xylenol with benzoyl chloride; 4-methylbenzyl benzoate (X), b.p. 136-138° at 0.5 mmHg (lit.,²⁴ 110° at 0.05 mmHg), from the triethylamine-catalysed reaction of 4-methylbenzyl alcohol with benzovl chloride; 2,5-dichlorophenyl benzoate (IIIa), m.p. 69° (lit.,¹⁷ 69°), from the triethylamine-catalysed reaction of 2,5-dichlorophenol with benzoyl chloride; methyl 2-phenylbenzoate, m.p. 115° (lit.,17 114-115°), from 2-phenylbenzoic acid and methanol; methyl 3-phenylbenzoate m.p. 160° (lit.,17 160°), from 3-phenylbenzoic acid and methanol. 2-Nitro-5-methylbiphenyl (VId), m.p. 86° (lit., 25 86-87°) was a specimen prepared by France, Heilbron, and Hey.²⁵

5-Chloro-2-methylbiphenyl (VIIb).—5-Chloro-2-methylaniline, m.p. 26° (lit., ¹⁷ 26-26.5°), was prepared by reduction of 5-chloro-2-methylnitrobenzene with tin and hydrochloric acid. The procedure of Cadogan 26 was used to convert 5-chloro-2-methylaniline into 5-chloro-2-methylbiphenyl (VIIb), a colourless oil, $n_{\rm p}^{20}$ 1.6000, b.p. 130–132° at

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5 mmHg (lit.,²⁷ 139-140° at 8 mmHg). The same procedure was also used to convert 5-nitro-2-chloroaniline into 5-nitro-2-chlorobiphenyl (XVa), m.p. 60° (lit., 28 59-60°).

2-Methoxy-5-nitrobiphenyl (XIVb).-2-Hydroxy-5-nitroaniline was converted into 2-methoxy-5-nitroaniline, m.p. 156° (lit.,²⁹ 160°), by reaction with ethereal diazomethane. The same procedure as before ²⁶ was then used to convert 2-methoxy-5-nitroaniline into 2-methoxy-5-nitrobiphenyl (XIVb), m.p. 93° (lit.,¹⁷ 95.2°).

Reactions of Benzoyl Peroxide with p-Disubstituted Benzenes.—Benzoyl peroxide (5 g) and the pure p-disubstituted benzene (100 g) were maintained at 80° (oil bath) for 72 h. The mixture was then cooled, dissolved in ether if semi-solid, extracted with saturated aqueous sodium hydrogen carbonate (5 \times 50 ml) to remove benzoic acid, and then washed with water. The combined extracts were washed with methylene chloride $(3 \times 50 \text{ ml})$, and these washings were added to the reaction mixture, which was then dried (MgSO₄). Acidification of the alkaline extracts precipitated benzoic acid, which was extracted into methylene chloride. The resultant solution was dried (MgSO₄), filtered, and evaporated to afford benzoic acid. The dried solution of the reaction mixture was concentrated by fractional distillation to leave a residue (ca. 20 g), which was made up to 50 ml with dry benzene. Portions of this solution were used in g.l.c. estimation of products.

p-Dichlorobenzene (Ia). G.l.c. analysis showed one major and one minor (<1%) component, with retention times corresponding to 2,5-dichlorobiphenyl (IIa) and 2,5-dichlorophenyl benzoate (IIIa), respectively. By the use of preparative g.l.c. (column D at 200°) the major component was isolated and shown to be identical with authentic 2,5-dichlorobiphenyl (IIa), $n_{\rm D}^{20}$ 1.6165 (lit.,² $n_{\rm D}^{20}$ 1.6167) (Found: C, 64.3; H, 3.5. Calc. for $C_{12}H_8Cl_2$: C, 64.7; H, 3.6%).

p-Dibromobenzene (Ib). G.l.c. analysis showed one major and one minor (<1%) component with retention times corresponding to 2,5-dibromobiphenyl (IIb) and 2,5-dibromophenyl benzoate (IIIb), respectively. By preparative g.l.c. (column D at 200°) the major component was isolated and identified as 2,5-dibromobiphenyl (IIb), $n_{\rm D}^{20}$ 1.6520, b.p. 120–130° at 0.5 mmHg (lit.,³⁰ 209° at 15 mmHg) (Found: C, 46.6; H, 2.7. Calc. for C₁₂H₈Br₂: C, 46·2; H, 2·55%).

p-Di-t-butylbenzene (Ic). G.l.c. analysis showed one major component which was isolated by preparative g.l.c. (column D at 200°) and identified as 2,5-di-t-butylbiphenyl (IIc), m.p. 95° (lit.,⁴ 94°) (Found: C, 90.35; H, 9.65. Calc. for $C_{20}H_{26}$: C, 90.2; H, 9.8%), τ 8.75 (s, 5-C(CH₃)₃) and 8.89 (s, 2-C(CH₃)₃). I.r. studies on the crude reaction product after removal of benzoic acid showed weak benzoate carbonyl absorption at 1730 cm⁻¹, suggesting that 2,5-di-t-butylphenyl benzoate (IIIc) was a minor product.

p-Dimethoxybenzene (Id). G.l.c. analysis showed one major component, which was isolated by preparative g.l.c. (column D at 200°) as an oil and identified as 2,5-dimethoxyphenyl benzoate (IIId) (Found: C, 69.6; H, 5.4. Calc. for (IIId) with aqueous 2N-sodium hydroxide gave benzoic acid

and 2,5-dimethoxyphenol, $n_{\rm D}^{20}$ 1.5478, b.p. 80° at 0.1 mmHg (lit.,⁵ 80-85° at 0.2 mmHg) (Found: C, 62.1; H, 6.3. Calc. for $C_8H_{10}O_3$: C, 62·3; H, 6·5%), ν_{max} 3450 (OH) cm⁻¹, τ 3·35 (s, OH) and 6·31 (s) and 6·38 (s) (OCH₃). The 2,5-dimethoxyphenol was characterised as 2,5-dimethoxyphenol tosylate, m.p. 98-100° (from ethanol) (Found: C, 58.0; H, 5.3. $C_{15}H_{16}O_5S$ requires C, 58.4; H, 5.2%). 6.31 (s) and 6.55 (s) (OCH₃), and 7.60 (s, CH₃).

p-Xylene (Va). G.l.c. analysis showed the presence of two major and two minor components with retention times corresponding respectively to 2,5-dimethylbiphenyl (VIa), 4,4'-dimethylbibenzyl (VIIIa), 2,5-dimethylphenyl benzoate (IX), and 4-methylbenzyl benzoate (X). With preparative g.l.c. (column D at 200°) the two major components were isolated and identified as 2,5-dimethylbiphenyl (VIa), $n_{\rm p}^{20}$ 1.5840, b.p. 110—115° at 5 mmHg (lit.,³¹ $n_{\rm p}^{20}$ 1.5819, b.p. 140° at 14.5 mmHg) (Found: C, 92.6; H, 7.2. Calc. for $C_{14}H_{14}$: C, 92.8; H, 7.2%), τ 7.71 (s, 5-CH₃) and 7.84 (s, $2-CH_3$), and 4,4'-dimethylbibenzyl (VIII), white crystals from ethanol, m.p. 84° (lit., 17 85°) (Found: C, 91.8; H, 8.35 Calc. for $C_{16}H_{18}$: C, 91.35; H, 8.65%), τ 7.22 (s, CH_2) and 7.75 (s, CH_3).

p-Chlorotoluene (Vb). G.l.c. analysis (column B at 200°) showed only one peak, but with column C two peaks were observed, suggesting the presence of two biphenyl derivatives, (VIb) and (VIIb). Preparative g.l.c. (column D at 200°) permitted isolation of both a mixture of these two components and an additional minor product. The mixture of 2-chloro-5-methylbiphenyl (VIb) and 2-methyl-5-chlorobiphenyl (VIIb) was obtained after purification by molecular distillation as a colourless oil, n_D^{20} 1.5984, b.p. 100° at 0.5 mm Hg (Found: C, 77.2; H, 5.8. Calc. for $C_{13}H_{11}Cl$: C, 77.0; H, 5.5%), τ 7.70 [s, CH₃ in (VIb)] and 7.84 [s, CH₃ in (VIIb)]. The retention time of the minor component corresponded to that of authentic 2-methyl-5-chlorobiphenyl (VIIb). The minor product from the preparative g.l.c. gave 4,4'-dichlorobibenzyl (VIIIb), m.p. 102° (from ethanol) (lit.,32 102°) (Found: C, 67·3; H, 4·9. Calc. for $C_{14}H_{12}Cl_2$: C, 66.9; H, 4.8%), τ 7.21 (s, CH_2).

p-Bromotoluene (Vc). G.l.c. analysis showed one major peak and one minor peak corresponding to [(VIc) and (VIIc)], and (VIIIc), respectively. A mixture of 2-bromo-5-methylbiphenyl (VIc) and 2-methyl-5-bromobiphenyl (VIIc) was isolated by preparative g.l.c. (column D at 200°), and obtained as a viscous liquid by molecular distillation, $n_{\rm D}^{20}$ 1.6145 (lit., ³³ $n_{\rm D}^{20}$ 1.6150 for 2-bromo-5-methylbiphenyl) (Found: C, 63.1; H, 4.4. Calc. for C₁₃H₁₁Br: C, 63.1; H, 4.5%). Since g.l.c. analysis gave only the total amount of bromomethylbiphenyls [(VIc) and (VIIc)], the integrated n.m.r. spectrum of the mixture was used in obtaining the ratio (VIc): (VIIc): τ 7.70 [s, 5-CH₃ in (VIc)] and 7.82 [s, 2-CH₃ in (VIIc)]. The presence of 4,4'-dibromobibenzyl (VIIIc) was confirmed by a comparison of retention time with that of an authentic specimen.

p-Nitrotoluene (Vd). G.l.c. analysis at 200° on column C showed one major peak; analysis on column B showed two major peaks corresponding to (VId) and (VIId), which were distinguished by comparison (retention time) with an

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authentic specimen of (VId). A mixture of 5-methyl-2-nitrobiphenyl (VId) and 2-methyl-5-nitrobiphenyl (VIId) was isolated by preparative g.l.c. (column D at 200°) as a yellow viscous oil (Found: C, 72.9; H, 5.2; N, 6.45. Calc. for $C_{13}H_{11}NO_2$: C, 73.1; H, 5.2; N, 6.55%), τ 7.60 [s, 5-CH₃ in (VId)] and 7.72 [s, 2-CH₃) in (VIId)].

Methyl p-toluate (Ve). G.I.c. analysis showed two major peaks corresponding to (VIe) and (VIIe). A mixture of methyl 4-methyl-2-phenylbenzoate (VIe) and methyl 4-methyl-3-phenylbenzoate (VIIe) was isolated by preparative g.I.c. and purified by molecular distillation (Found: C, 79·2; H, 6·4. $C_{15}H_{14}O_2$ requires C, 79·6; H, 6·2%), τ 6·48 (s, CO_2CH_3) and 7·61 (s, CH_3 [in (VIe)] and 6·15 (s, CO_2CH_3) and 7·63 (s, CH_3) [in (VIIe)]. The proportions of (VIe) and (VIIe) in the mixture were determined from the integrated spectrum [cf. τ 6·48 (s, CO_2CH_3) in methyl ophenylbenzoate; and 6·15 (s, CO_2CH_3) in methyl m-phenylbenzoate].

p-Methoxytoluene (XI). G.l.c. analysis showed one major and two minor peaks. The two minor components were identified, by comparison of the g.l.c. retention times with those of authentic specimens, as 4,4'-dimethoxybibenzyl $[\tau \ 7.22 \text{ (s, } CH_2)]$ and 4-methoxybenzyl benzoate $[\tau \ 4.79$ (s, CH_2 ·O·COPh)]. The major component was isolated by preparative g.l.c. (column D at 200°) and purified by molecular distillation to afford 2-methoxy-5-methylphenyl benzoate (XII), b.p. 130—140° at 0·1 mmHg, $n_{\rm D}^{20}$ 1·5613 (Found: C, 73·9; H, 6·2. $C_{15}H_{14}O_3$ requires C, 74·35; H, 5·8%), τ 6·32 (s, OCH₃) and 7·75 (s, CH₃). The aromatic pattern of the expanded n.m.r. spectrum, when compared with the spectra of o- and m-tolyl benzoates, and o- and m-methoxyphenyl benzoates resembled more closely those of *m*-tolyl benzoate and o-methoxyphenyl benzoate. Alkaline hydrolysis of 2-methoxy-5-methylphenyl benzoate (XII) afforded 3-hydroxy-4-methoxytoluene, m.p. 38° (lit.,¹⁷ 37-39°), which on treatment with hydrogen iodide gave 3,4-dihydroxy-toluene, m.p. 65° (lit.,¹⁷ 65°). In one anomalous reaction, when the reaction mixture, after removal of free benzoic acid, was left for 2 months, 2-hydroxy-5-methylphenylbenzoate, m.p. 166° (from benzene), precipitated (Found: C, 73·49; H, 5·24. $C_{14}H_{12}O_3$ requires C, 73·67; H, 5·30%), ν_{max} 3400 (OH) and 1730 (>C=O) cm⁻¹. There was no indication of an ether linkage in the 1150-1060 cm⁻¹ range. τ 2.80 (s, OH), 1.70–1.95 (m, aromatic H ortho to >C=O), 2.20-3.20 (m, aromatic H), and 7.80 (s, CH_3). The expanded aromatic region of the n.m.r. spectrum resembled more closely that of *m*-tolyl benzoate than that of o-tolyl benzoate.

p-Chloronitrobenzene (XIIIa). G.l.c. analysis showed the presence of two major components. Preparative g.l.c. on column D at 200° yielded a mixture of 5-chloro-2-nitrobiphenyl (XIVa) and 2-chloro-5-nitrobiphenyl (XVa) (Found: C, 61·4; H, 3·5. Calc. for $C_{12}H_8CINO_2$: C, 61·8; H, 3·45%). The two components were identified from the retention time of the isomer present in smaller amount, which corresponded to that of 2-chloro-5-nitrobiphenyl (XVa).

p-Nitroanisole (XIIIb). G.1.c. showed the presence of two major components. Preparative g.l.c. did not afford a sample mixture of 2-methoxy-5-nitrobiphenyl (XIVb) and 5-methoxy-2-nitrobiphenyl (XVb) without excessive contamination with p-nitroanisole (XIIIb). The isomer present in smaller amount had a retention time corresponding to that of 2-methoxy-5-nitrobiphenyl (XIVb).

Methyl p-methoxybenzoate (XIIIc). G.l.c. analysis

showed two major components. Preparative g.l.c. on column L at 200° always yielded a sample of a mixture of methyl 4-methoxy-2-phenylbenzoate (XIVc) and methyl 4-methoxy-3-phenylbenzoate (XVc) contaminated with methyl p-methoxybenzoate (XIIIc) [Found: C, 69.95; H, 5.9. Calc. for $C_9H_{10}O_3$ (XIIIc): C, 65.05; H, 6.1. Calc. for $C_{15}H_{14}O_3$ (XIVc and XVc): C, 74.35; H, 5.8. Calc. for $C_{16}H_{14}O_5$ (benzoyloxylated XIIIc): C, 67.1; H, 4.9%]. This analysis is consistent only with a mixture of starting material (XIIIc) together with the phenylated products (XIVc) and (XVc). It is not consistent with a mixture of starting material (XIIIc) and benzoyloxylated products.

Reactions of Benzoyl Peroxide with Sulphides and Sulphoxides.—In all reactions the sulphide or sulphoxide (50 g) and benzoyl peroxide (5 g) were mixed and kept at 80° for 72 h; the product was then worked up by the usual procedure.

Methyl phenyl sulphide (XVIa). The initial addition of benzoyl peroxide to the sulphide (XVIa) at 80° caused a vigorous reaction with decrepitation. The i.r. spectrum of the crude product showed absorptions at 1780s and 1715m (C=O of benzoic anhydride), 1720s (C=O of benzoate), and 1050 (sulphoxide) cm⁻¹. G.l.c. showed two distinct major peaks and an indistinct peak. The latter corresponded to benzoic anhydride and one of the others to methyl phenyl sulphoxide (XVIIa). A sample of the reaction mixture was chromatographed on alumina (Laporte H, 100-120 mesh) with light petroleum-benzene as eluant. After elution of methyl phenyl sulphide (XVIa) an oil was obtained, ν_{max} 1720 (>C=O) cm⁻¹, τ 1·80—2·10 (m, aromatic *H* ortho to >C=O), 2·40—3·00 (m, aromatic *H*), and 4·40 (s, S·CH₂). Vacuum sublimation gave a colourless oil, phenylthiomethyl benzoate (XVIIIa), consistent with these spectral properties (Found: C, 68.5; H, 5.0. C₁₄H₁₂O₂S requires C, 68.85; H, 4.9%). Further elution with methylene chloride gave methyl phenyl sulphoxide (XVIIa), identical with an authentic specimen, after purification by vacuum sublimation, m.p. 31° (Found: C, 60.4; H, 5.9. Calc. for C₇H₈OS: C, 60.0; H, 5.75%), $\nu_{max.}$ 1050 (sulphoxide) cm⁻¹, τ 2.30—2.70 (m, aromatic H) and 7.55 (s, $SOCH_3$). Benzoic acid (1.69 g) was isolated in the extraction procedure. By use of g.l.c. analysis (column C at 200°; bibenzyl as marker) the following estimations of yield were made: (XVIIa), 1.135 g; (XVIIIa) 1.614 g; and benzoic anhydride, 1.77 g.

Methyl p-tolyl sulphide (XVIb). The initial addition of benzoyl peroxide to the sulphide at 80° caused a vigorous reaction with decrepitation. As with methyl phenyl sulphide (XVIa), the i.r. spectrum of the crude product showed absorptions due to benzoate, anhydride, and sulphoxide groupings. A sample of the crude product was chromatographed on alumina (Laporte H) with light petroleum-benzene as eluant. After initial elution of unchanged sulphide (XVIb), further elution gave p-tolylthiomethyl benzoate (XVIIIb), m.p. 42° (from light petroleum) (Found: C, 69.75; H, 5.4. $C_{15}H_{14}O_2S$ requires C, 69.75; H, 5.45%). ν_{max} 1720 (>C=O) cm⁻¹, τ 1.80—2.10 (m, aromatic *H ortho* to >C=O), 2.40—3.00 (m, aromatic H), 4.46 (s, S·CH₂·O·-COPh), and 7.70 (s, CH_3). Elution with methylene chloride gave methyl p-tolyl sulphoxide (XVIIb), m.p. 51° (lit.,17 51°) (Found: C, 62·2; H, 6·3. Calc. for $C_8H_{10}OS$: C, 62·3; H, 6.5%), ν_{max} 1050 (sulphoxide) cm⁻¹, τ 2.30–2.90 (2d, J 9 Hz, aromatic H), 7.55 (s, SOCH₃), and 7.80 (s, CH_3). Benzoic acid (1.54 g) was isolated in the extraction procedure.

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G.l.c. analysis (column C at 200° ; bibenzyl as marker) gave the following product yields: (XVIIb), 1.318 g; (XVIIIb), 1.76 g; and benzoic anhydride, 1.86 g.

Methyl p-tolyl sulphoxide (XVIIb). The i.r. spectrum of the crude product showed absorptions due to anhydride, benzoate, sulphoxide, and sulphone groupings. G.l.c. analysis on column C at 200° showed the presence of three major products and a minor product. Column chromatography on alumina (Laporte H) with light petroleum as eluant gave an unidentified yellow oil, v_{max} , 1490 and 800 cm⁻¹, $\tau 2.60-3.10$ (m, aromatic H), 5.92 (s, ?), and 7.80 (s, CH₃) (Found: C 69.7; H, 6.5; S, 23.4%). This corresponded in retention time to the minor product. Elution with benzene gave an oil, purified by vacuum sublimation to afford p-tolylsulphinylmethyl benzoate (XX) as a colourless oil, b.p. 120° at 0.1 mmHg, $n_{\rm D}^{20}$ 1.5958 (Found: C, 65.9; H, 4.8. C₁₅H₁₄O₃S requires C, 65.7; H, 5.15%), $v_{\rm max}$, 1720

(>C=O) cm⁻¹, τ 1·80—2·10 (m, aromatic *H* ortho to >C=O), 2·40—3·10 (m, aromatic *H*), 4·52 (s, SO·CH₂·O·COPh), and 7·78 (s, CH₃). Elution with diethyl ether yielded methyl *p*-tolyl sulphone (XIX), m.p. 89° (from light petroleum– benzene) (lit.,¹⁹ 89°), v_{max} . 1330 and 1150 (SO₂) cm⁻¹, τ 2·10 and 2·90 (2d *J* 9 Hz, aromatic *H*) 7·12 (s, SO₂CH₃), and 7·60 (s, CH₃) (Found: C, 56·85; H, 6·0. Calc. for C₃H₁₀O₂S: C, 56·45; H, 5·9%). Benzoic acid (2·40 g) was isolated in the extraction procedure. G.l.c. analysis did not permit any accurate estimation of products, owing to serious overlapping of peaks, but at least 1 g each of (XX), (XIX), and benzoic anhydride was formed.

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