Aromatic Substitution. Part XXII.¹ Polarity of Aryl Radicals

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The rates of substitution of anisole relative to benzene by aryl radicals generated from diazonium tetrafluoroborates and pyridine in homogeneous solution have been measured and follow, qualitatively, the order expected on the basis of the theory of polarised aryl radicals. The substituent in the radical affects its permanent polarisation. Apparent contradictions in the literature concerning the behaviour of anisole as a substrate and the polarity of the p-methoxyphenyl radical are resolved by the use of this source of free radicals. p-Methoxyphenyl is more nucleophilic than phenyl as expected. m-Methoxyphenyl is no more electrophilic than phenyl and an explanation is suggested. p-Tolyl is more nucleophilic than expected on the basis of σ_{p-Me} .

WHILE aryl free-radicals are uncharged, substituents can affect the polarity of the radicals, rendering them more electrophilic or nucleophilic when compared with the unsubstituted phenyl radical itself.² It was further suggested that the radical polarity was affected only by the permanent polarisation of the substituent and not by any polarisability effects which that substituent may exert during reactions.³ This will have to be modified slightly to consider the permanent polarisation of the substituent in the aryl radical and not its precursor in which the σ -orbital is fully occupied.

There is much evidence ⁴ in support of the ' theory of polarised radicals.' The total rate ratios for the arylation of nitrobenzene by substituted aryl radicals showed

of the values in Table 1 are higher than those obtained by other workers using diaryl peroxides and this has been attributed⁵ to differences in reaction temperatures. Simamura et al.^{5e} plotted log ${}^{\mathbf{X}}F_m$ against $\sigma m_{\cdot \mathbf{X}}$ and obtained straight lines with slopes -0.81 for p-nitrophenylation, -0.27 for p-chlorophenylation, 0.05 for phenylation, 0.03 for p-tolylation, and 0.09 for pmethoxyphenylation. Negative slopes were interpreted as due to radicals more electrophilic, and positive slopes due to radicals more nucleophilic, than the phenyl radical. Some points fell well off the lines: $^{nitro}_{II}K$ - $(p-\text{MeO-C}_6\text{H}_4) = 3.94$ and ${}^{\text{MeO}}_{\text{H}}K(p-\text{MeC}_6\text{H}_4) = 1.85$ suggest that both of these radicals are more electrophilic than Ph. itself. The concept of polarised radicals was

TABLE 1

Total rate ratios in the arylation of substituted benzene derivatives with p-substituted aryl radicals (from N-nitrosoacetanilides) at 20° ⁵

Substrate	$\mathbf{x}_{\mathbf{H}}K$	p-NO₂•C ₆ H₄•	p-Cl·C ₆ H ₄ ·	C ₆ H₅∙	p-Me·C ₆ H ₄ ·	p-MeO·C ₆ H ₄ ·
PhNO.	$\mathbf{nitro}_{\mathbf{H}}K$	0.68	2.69 a	5.02	5.50	3.94
PhOMe	$MeO_{H}K$	2.39	1⋅88 ه	1.71	1.85	1.79
PhMe	Me_HK	1.80	1.56	1.68	1.65	1.56
PhCl	$ci_{\mathbf{H}}K$	0.89	1.41	1.61	1.57	1.92
			۵ At 18°			

that electron-withdrawing substituents gave values of $\operatorname{nitro}_{\mathrm{H}} K$ lower than that for attack by Ph·, while electron donating substituents gave $^{nitro}_{H}K$ greater than that for Ph. The only exception appeared to be the pmethoxyphenyl radical. The p-methoxy-group has $+M > -I(\sigma_{p-MeO} = -0.268)$ so that $p-MeOC_{g}H_{4}$. should be more nucleophilic than Ph. ^{nitro}_HK- $(p-MeO \cdot C_6H_4 \cdot)$ was, however, slightly lower than $^{nitro}_{H}K(Ph)$ when peroxides were used as the radical sources.^{3a} The polarity of aryl radicals was further investigated by Simamura and his co-workers⁵ who used p-substituted N-nitrosoacetanilides as their radical sources and a variety of substrates (Table 1). Most

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extended to include ortho-substituted phenyl radicals,^{6,7} but steric hindrance to attack at the ortho-position had to be invoked. To avoid steric factors due to substituents in the substrate the arylation of pyridine was studied;^{8,9} the total rate ratios (Table 2) agreed with the concept of polarised radicals and with the known behaviour of pyridine towards electrophilic and nucleophilic reagents. Both methoxyphenyl radicals were more nucleophilic than phenyl. Contrary to expectations based on σ -constants the p-tolyl radical appears to be more nucleophilic than p-methoxyphenyl.

¹ Part XXI. R. A. Abramovitch, F. Helmer, and M. Liveris,

<sup>J. Org. Chem., in the press.
² G. H. Williams, 'Homolytic Aromatic Substitution,'</sup> Pergamon Press, Oxford, 1960, p. 22, summarises earlier work.
³ (a) J. K. Hambling, D. H. Hey, and G. H. Williams, J. Chem. Soc., 1960, 3782; 1962, 487; (b) J. K. Hambling, D. H. Hey, S. Orman, and G. H. Williams, *ibid.*, 1961, 3108.
⁴ D. H. Hey, in 'Advances in Free-Radical Chemistry,' ed. C. H. Williams, vol. 2, Lorgos Press, London, 1967, p. 62.

G. H. Williams, vol. 2, Logos Press, London, 1967, p. 62.

⁵ (a) T. Inukai, K. Kobayashi, and O. Simamura, Bull. Chem. Soc. Japan, 1962, **35**, 1576; (b) T. Migita, N. Morikawa, and O. Simamura, *ibid.*, 1963, **36**, 980; (c) R. Itó, T. Migita, N. Morikawa, and O. Simamura, *ibid.*, p. 985; (d) *ibid.*, p. 992; (a) Tatakadam, 1965, 91, 955; (d) *ibid.*, p. 992; (e) Tetrahedron, 1965, **21**, 955. ⁶ D. H. Hey, H. N. Moulden, and G. H. Williams, J. Chem.

Soc., 1960, 3769. 7 D. H. Hey, S. Orman, and G. H. Williams, J. Chem. Soc.,

^{1965, 101.}

⁸ R. A. Abramovitch and J. G. Saha, J. Chem. Soc., 1964, 2175.

⁹ R. A. Abramovitch and M. Saha, J. Chem. Soc. (B), 1966, 733.

Arguments have been presented against the theory of polarised radicals. On the basis of results of arylations of anisole with aroyl peroxides at 80° and p-nitro-Nnitrosoacetanilide at 21° (Table 3) it was concluded ^{10c}

TABLE 2

Total rate ratio in the arylation of pyridine at 40° (Gomberg-Hey conditions) 8,9

Radical	$Py_{Benz}K$	Radical	$Py_{Benz}K$
Ph•	1.14	o-Me·C ₆ H ₄ ·	1.72
o-MeO·C ₆ H₄•	1.27	p-Me·C ₆ H ₄ ·	1.44
p-MeO•C ₆ H ₄ •	1.30	o-NO, C, H,	0.47
o-Br•C ₆ H₄•	0.70	p-NO, C, H,	0.78
p-Br•C ₆ H₄•	0.87		

TABLE 3

Arylation of anisole 10

Aryl radical	$MeO_{\mathbf{H}}K$	Ref.
p-Me·C _e H ₄ ·	2.65	10a
C ₆ H ₅ ·	2.02	10b
p-NO₂•C ₆ H₄•	2.03	10c
p-NO2 C6H4 ·	$2 \cdot 20$	10c
p-NO2 C6H4.	1.75	10c
p-NO2 C6H4	2.81	10d

^a From *p*-nitro-*N*-nitrosoacetanilide at 21°. ^b Calculated for 80° from the data obtained as under footnote ^a (sum of partial rate factors). c At 100°.

that the p-nitrophenyl radical behaved towards anisole 'very little differently from the phenyl radical,' and that the p-tolyl radical 'gives in a modest way some of the results predicted for *p*-nitrophenyl radical.' Arylation of anisole with diaroyl peroxides was, however, only a small fraction of the total reaction, the main products being those of benzoyloxylation.^{10c} Results obtained in the arylation of nitrobenzene with mixed diaryl peroxides were also said to speak against the concept of polarised radicals.¹¹

From the above it seems clear that some ambiguities can arise when diaroyl peroxides or N-nitrosoacetanilides are used as the radical source, particularly in those cases when the substrate is anisole or when the attacking radical contains a methoxy-substituent. It has recently been shown 12 that the pyridine-catalysed decomposition of benzenediazonium tetrafluoroborate in an aromatic solvent¹³ and sulpholan gives quantitative data which appear to be more reliable than those obtained with benzoyl peroxide, particularly since benzoyloxylation cannot intervene as a side-reaction. It was therefore decided to re-investigate the homolytic arylation of anisole in homogeneous solution with aryldiazonium tetrafluoroborates and pyridine as the radical source.

Authentic samples of the required disubstituted biphenyls were usually prepared by an Ullmann reaction

J. Chem. Soc. (B), 1969

followed by preparative gas-chromatographic separation of the products. A number of products so obtained had physical properties different from those in the literature. Thus, m.p. of 63-64° has been recorded ^{5c} for 2-methoxy-4'-nitrobiphenyl. Our product from both the reaction of o-iodoanisole with p-iodonitrobenzene and the decomposition of p-nitrobenzenediazonium tetrafluoroborate in anisole had m.p. 50-51°, and gave the expected mass spectral fragmentation and n.m.r. and infrared spectra. 3-Methoxy-4'-methylbiphenyl, obtained both from *m*-iodoanisole and p-iodotoluene and from p-tolyldiazonium tetrafluoroborate and anisole, was a liquid, b.p. $96^{\circ}/0.8$ mm., but was reported ^{5d} to be a solid, m.p. 80°. Again, the i.r., n.m.r., and mass spectra of our product were consistent with the expected structure. 2,3'-Dimethoxybiphenyl, m.p. 39-40°, was obtained both via the Ullmann reaction and from the appropriate diazonium salt. The product obtained by the quinoline and copper-chromite decarboxylation of 5,6'-dimethoxybiphenyl-2,2'-dicarboxylic acid was reported ¹⁴ to have m.p. 79-80°. The spectroscopic and analytical data all agreed with those expected for our product.

2and 4-Methoxy-4'-methylbiphenyls were synthesised from the appropriate methoxyphenyl-lithium and 4-methylcyclohexanone. The tertiary alcohols were dehydrated and dehydrogenated by heating with sulphur and zinc.



When p-methylbenzenediazonium tetrafluoroborate was decomposed in anisole in the presence of an equivalent of pyridine, 4-methyldiphenyl ether was formed in low yield in addition to the isomeric methoxymethylbiphenyls. It could also be prepared from sodium phenoxide and p-iodotoluene in the presence of copper. *m*-Methoxydiphenyl ether was also isolated from the reaction of *m*-methoxybenzenediazonium tetrafluoroborate and anisole and was prepared from sodium phenoxide and *m*-iodoanisole.

Isomer ratios were determined by decomposing the aryldiazonium tetrafluoroborate in anisole in the presence of pyridine. A suitable solvent was added to effect homogeneity; sulpholan was the most convenient. The products were analysed quantitatively by gas chromatography. Competitive experiments were carried out with benzene as the reference compound. The phenylation of mixtures of toluene and benzene

 ¹⁰ (a) A. Cain, Ph.D. Thesis, New York University, 1962;
 (b) J. Cazes, Ph.D. Thesis, New York University, 1963; (c) A. Rossi, Ph.D. Thesis, New York University, 1964; (d) R. F. Sweeney, Ph.D. Thesis, New York University, 1965.
 ¹¹ M. Mingin and K. H. Pausacker, Austral. J. Chem., 1965,

^{18, 821.}

¹² R. A. Abramovitch and O. A. Koleoso, J. Chem. Soc. (B), 1968, 1292.

¹³ R. A. Abramovitch and J. G. Saha, Tetrahedron, 1965, 21, 3297.

¹⁴ S. Yu. Yunosov and F. F. Ismailov, Zhur. obshchei Khim., 1960, 30, 1721; Chem. Abs., 1961, 55, 3632a.

under these conditions proceeds without evidence of preferential solvation by one of the solvents.¹² To ensure that this was so with the other radicals used the arylations were carried out with various molar ratios (4:1, 1:1, and 1:4) of anisole: benzene with one equivalent of pyridine, and a 1:1 ratio with three equivalents of pyridine. While the value of $MeO_{\mathbb{H}}K$ - $(p-\text{Me-C}_6H_4)$ remained fairly constant, the value of $^{MeO}_{H}K(\phi - MeO \cdot C_{6}H_{4} \cdot)$ when 1 : 1 molar ratio of substrate and one equivalent of pyridine was used was not consistent with the value of σ_{p-MeO} (see Discussion). It was suspected that here, indeed, non-statistical distribution of the diazonium salt could be occurring and experiments were carried out with anisole: benzene molar ratios of 1:1, 3:1, 4:1, 1:3, and 1:4, different amounts of pyridine (0, 1, and 3 molar equivalents), and different solvents (acetonitrile and sulpholan). The decomposition of p-methoxybenzenediazonium tetrafluoroborate in anisole-benzene in the absence of pyridine was effected to determine whether the experiments with one or three equivalents of pyridine involved the participation of both free aryl radicals and biradical cations.¹⁵ The values of $MeO_{H}K(p-MeO \cdot C_{6}H_{4})$ obtained with one equivalent of pyridine (1:1 solvent ratio) was intermediate between those obtained in the absence of pyridine or with a large benzene : anisole ratio and those obtained with three equivalents of pyridine or with a larger proportion of anisole. No such phenomenon was observed in the p-nitrophenylation, p-chlorophenylation, or *m*-methoxyphenylation.

EXPERIMENTAL

I.r. spectra were measured on Perkin-Elmer 21 and Beckman IR 8 spectrometers equipped with sodium chloride optics. N.m.r. spectra were measured on Varian A-60 and HA-100 instruments in carbon tetrachloride with tetramethylsilane as internal standard. Mass spectra were determined with an MS-12 single-focusing instrument.

Reagents.-These were purified by standard procedures.12

Reference Compounds.—3- and 4-Methoxybiphenyl and 4-chlorobiphenyl were prepared by the decomposition of the appropriate solid diazonium tetrafluoroborate in benzene in the presence of 1 equiv. of pyridine at 60° ,¹³ and had b.p. $110^{\circ}/3$ mm., m.p. 88—89°, and m.p. 74—75°, respectively. 4-Methyldiphenyl ether, prepared as described by Hickinbottom,¹⁶ had b.p. 117°/3 mm. (lit.,¹⁷ b.p. 277—278°/745 mm.); n.m.r. spectrum: 9H multiplet at τ 3·0, 3H singlet at τ 7·7. 3-Methoxydiphenyl ether was similarly prepared from sodium phenoxide and *m*-iodoanisole and had b.p. 135°/3 mm. (lit.,¹⁷ b.p. 303°/745 mm.).

2-Methoxy-4'-nitrobiphenyl.—A solution of o-iodoanisole $(1\cdot 0 \text{ g.})$ and p-iodonitrobenzene $(2\cdot 0 \text{ g.})$ in dimethylformamide (5 ml.) was heated to boiling, copper-bronze $(2\cdot 5 \text{ g.})$ was added, and the mixture was heated under reflux with stirring for 4 hr. More copper-bronze $(2\cdot 5 \text{ g.})$ was added and heating continued for 4 hr. The cold mixture was poured into water, filtered, and the solid extracted with

¹⁶ W. J. Hickinbottom, 'Reactions of Organic Compounds,' 3rd edn., Longmans, Green and Co., London, 1957, p. 116. 781

boiling acetone (4 × 50 ml.). Evaporation of the solvent and fractional vacuum distillation gave first 2,2'-dimethoxybiphenyl (36 mg.) [which, after recrystallisation from methanol, had m.p. 155—156° (lit.,¹⁸ m.p. 155°)] and a mixture of 2-methoxy-4'-nitrobiphenyl and 4,4'-nitrobiphenyl. The mixture was resolved by g.l.c. on a 2 ft. × 4 in. column packed with Apiezon L (20%) on Gas Chrom P (100—120 mesh) at 200° and a helium flow rate of 80 ml./ min. The second peak (retention time 28 min.) was due to 4,4'-dinitrobiphenyl, m.p. 240° (from methanol) (lit.,¹⁸ m.p. 238—239°). The first peak (retention time 18 min.) was due to 2-methoxy-4'-nitrobiphenyl, m.p. 50—51° (lit.,^{5c} m.p. 63—64°); mass spectrum: M^+ , 229; $(M - NO)^+$, 199; $(M - NO_2)^+$, 183; $(M - NO - CH_3O)^+$, 168.

3-Methoxy-4'-nitrobiphenyl.—This was prepared as described for 2-methoxy-4'-nitrobiphenyl but from miodoanisole (1.0 g.). The acetone extract was vacuumdistilled and the distillate resolved by g.l.c. but at a column temperature of 235°. 3,3'-Dimethoxybiphenyl, m.p. 30° (lit.,¹⁸ m.p. 36°), 3-methoxy-4'-nitrobiphenyl, m.p. 89—90° (lit.,⁵⁶ m.p. 90—91°), and 4,4'-dinitrobiphenyl, m.p. 240°, were resolved in that order.

4-Methoxy-4'-nitrobiphenyl.—Fractional distillation of the products of the reaction of p-iodoanisole (1.0 g.) and p-iodonitrobenzene (2.0 g.) gave a semi-solid [from which 4,4'-dimethoxybiphenyl crystallised and was fractionally crystallised from methanol and had m.p. 171—172° (lit.,¹⁸ m.p. 173°)] and 4,4'-dinitrobiphenyl, m.p. 240°. The methanol mother liquors were concentrated and the residue purified by g.l.c. (conditions as above) to give the biphenyl, m.p. 108—109° (from methanol) (lit.,^{5c} m.p. 110—111°).

2-(1'-Hydroxy-4'-methylcyclohexyl)anisole.o-Bromoanisole (9 g.) in dry ether (5 ml.) was added during $\frac{1}{2}$ hr. at 5° to a solution of *n*-butyl-lithium [from lithium (1·1 g.) and n-butyl bromide (10 g.) in dry ether (90 ml.)]. After 1 hr. during which the stirred solution was allowed to reach room temperature, 4-methylcyclohexanone (8 g.) in ether (5 ml.) was added during $\frac{1}{2}$ hr. The mixture was stirred at room temperature for 4 hr., poured into ice-cold water (200 ml.), and steam-distilled to remove unchanged starting materials. The residue was extracted with ether $(2 \times$ 100 ml.), the extract dried (MgSO₄), and evaporated and the residue distilled under vacuum to give 2-(1'-hydroxy-4'methylcyclohexyl)anisole (7.6 g.), b.p. 126°/3 mm. [Found: C, 76.4; H, 9.3%; M (mass spec.), 220. C₁₄H₂₀O₂ requires C, 76·3; H, 9·15%; M, 220]; ν_{max} (liquid film) (main peaks only): 3560s, 3460w, 1595m, 1580m, 1480s, 1450s, 1430s, 1390m, 1290m, 1220s, 1020s, 990s, and 745s cm.⁻¹. N.m.r. spectrum (at 60 Mc./sec.): 7 3.0 (4H multiplet, Ar-H), τ 6.1 (3H singlet), τ 6.8 (1H singlet), τ 8.2 (5H broad singlet), $\tau 8.4$ (4H singlet), $\tau 9.1$ (3H singlet).

2-Methoxy-4'-methylbiphenyl.—The above alcohol (2.0 g.) was heated under reflux with sulphur (1.0 g.) for 4 hr. Zinc dust (0.1 g.) was then added and the mixture was heated for another hour. It was then extracted with ether $(3 \times 20 \text{ ml.})$, dried (MgSO₄), and evaporated and the residue distilled to give the biphenyl, b.p. $80^{\circ}/0.1 \text{ mm.}$ Recrystallisation from methanol gave the pure product (0.29 g.), m.p. 79— 80° (lit., ^{5c} m.p. 83°).

3-Methoxy-4'-methylbiphenyl.—This was prepared from

¹⁵ R. A. Abramovitch and F. F. Gadallah, J. Chem. Soc. (B), 1968, 497.

 ¹⁷ Heilbron's 'Dictionary of Organic Compounds,' ed. J. R. A.
 Pollock and R. Stevens, Eyre and Spottiswoode, London, 1965.
 ¹⁸ 'Handbook of Chemistry and Physics,' ed. R. C. Weast,

S. M. Selby, and C. D. Hodgman, 46th edn., The Chemical Rubber Co., Ohio, 1966.

m-iodoanisole (0.6 g.) and *p*-iodotoluene (1.2 g.) in sulpholan (5 ml.) with copper-bronze (4 g.). The product was vacuum-distilled and the distillate solidified on cooling. Crystallisation from methanol gave 4,4'-dimethylbiphenyl (48 mg.), m.p. 125° (lit.,¹⁸ m.p. 125°). The methanol mother liquors were evaporated and the residue analysed by g.l.c. on a 4 ft $\times \frac{1}{4}$ in. column packed with Apiezon L (25%) on Chromosorb W (60-80 mesh) at 180° with a helium flow rate of 60 ml./min. 3,3'-Dimethoxybiphenyl, m.p. 34°, had a retention time of 73 min. 3-Methoxy-4'methylbiphenyl was obtained as a colourless liquid, b.p. 96°/0.8 mm. (lit.,^{5d} m.p. 80°) [Found: C, 84.7; H, 7.15%; M, (mass spec.) 198. Calc. for $C_{14}H_{14}O$: C, 84.8; H, 7.1%; M, 198]; v_{max.} (liquid film): 3030m, 2920m, 2820m, 1595s, 1565m, 1515m, 1480s, 1430m, 1400w, 1295s, 1260w, 1220s, 1210s, 1175m, 1170m, 1050m, 1025m, 1010m, 810s, 765s, and 680s cm.⁻¹; n.m.r. (100 Mc./sec.): $\tau 2.6$ (2H doublet, J 4 c./sec.), $\tau 2.75$ —3.00 (5H complex multiplet), $\tau 3.25$ (1H multiplet), $\tau 6.2$ (3H singlet), and $\tau 7.6$ (3H singlet). The mass spectrum had small peaks at m/e 183 $(M - 15)^+$ and m/e 167 $(M - 31)^+$ corresponding to the loss of CH₃ and CH₃O fragments from the parent compound. The M^+ ion was the base peak.

4-(1'-Hydroxy-4'-methylcyclohexyl)anisole.—The procedure was as described for the 2-isomer except that p-bromoanisole (9.0 g.) was used, giving the anisole (9 g.), m.p. 69—70° (from methanol) [Found: C, 76·1; H, 9·0%; M, (mass spec.) 220. $C_{14}H_{20}O_2$ requires C, 76·3; H, 9·15%; M, 220]; ν_{max} . (KBr disc) (main peaks): 3440s, 2930s, 2860s, 1510s, 1450s, 1240s, 1170s, 1030s, 990m, and 820s cm.⁻¹; n.m.r. (60 Mc./sec.): τ 2·8 (2H doublet, J 9 c./sec.), τ 3·3 (2H doublet, J 9 c./sec.), τ 4·1 (1H singlet), τ 6·3 (3H singlet), τ 7·7 (4H broad singlet), τ 8·25 (5H broad singlet), τ 9 (3H doublet).

4-Methoxy-4'-methylbiphenyl.—The alcohol (1.0 g.) was heated with sulphur (0.5 g.) for 4 hr.; zinc dust (0.05 g.) was added, and heating continued for 1 hr. The mixture was extracted with ether (2×10 ml.), dried (MgSO₄), evaporated, and the residue vacuum-distilled to give the biphenyl (0.1 g.), m.p. 111—112° (lit.,^{5c} m.p. 111°).

2,4'-Dimethoxybiphenyl.—This was prepared from oiodoanisole (2 g.) and p-iodoanisole (2 g.) in sulpholan (10 ml.). The product was distilled to give a semi-solid from which 2,2'-dimethoxybiphenyl (0.11 g.), m.p. 155° (lit.,¹⁸ m.p. 155°) and 4,4'-dimethoxybiphenyl (0.10 g.), m.p. 174°, were fractionally crystallised from methanol. The combined mother liquors were evaporated and vacuum distilled at 126°/0.3 mm. to give 2,4'-dimethoxybiphenyl (20.8 mg.), m.p. 69—70° after recrystallisation (lit.,^{5e} m.p. 64°) from methanol.

3,4'-Dimethoxybiphenyl.—The product from the reaction of m-iodoanisole (0.94 g.) and p-iodoanisole (0.94 g.) was distilled under vacuum to give a semi-solid from which 4,4'dimethoxybiphenyl (75.0 mg.), m.p. 173°, was separated by crystallisation from methanol. The filtrate was evaporated and resolved by g.l.c. on a 6 ft. $\times \frac{1}{4}$ in. column packed with Apiezon L (25%) on Chromosorb W (60—80 mesh) at 190° and a helium flow rate of 60 ml./min. 3,3'-Dimethoxybiphenyl, m.p. 32—33°, had a retention time of 70 min. 3,4'-Dimethoxybiphenyl, m.p. 57—58° (lit.,^{5c} m.p. 60—61°), had a retention time of 75 min.

2,3'-Dimethoxybiphenyl.—The product from the reaction of o-iodoanisole (1.0 g.) and m-iodoanisole (1.0 g.) was dissolved in acetone and the solution concentrated whereupon 2,2'-dimethoxybiphenyl (74 mg.), m.p. $154-155^{\circ}$

J. Chem. Soc. (B), 1969

(from methanol) (lit.,¹⁸ m.p. 155°), separated. The filtrate was concentrated and resolved by g.l.c. as above to give 3,3'-dimethoxybiphenyl, m.p. 32—33°, and 2,3'-dimethoxybiphenyl (retention time 45 min.), m.p. 39—40° (lit.,¹⁴ m.p. 79—80°); $\nu_{\rm max}$ (KBr disc): 3060w, 3000w, 2940m, 2830m, 1590s, 1575s, 1490m, 1470s, 1450s, 1410s, 1255s, 1230s, 1200s, 1170s, 1110s, 1040s, 1010s, 850s, 770s, 740s, and 690s cm.⁻¹; mass spectrum: m/e 214 (M^+) base peak, m/e 199 (M - 15)⁺, m/e 184 (M - 30)⁺, m/e 183 (M - 31)⁺.

4-Chloro-2'-methoxybiphenyl.—Prepared from o-iodoanisole (1.0 g.) and p-chloroiodobenzene (1.0 g.) in sulpholan (10 ml.), the product was distilled under vacuum and subjected to g.l.c. on a 4 ft. $\times \frac{1}{4}$ in. column packed with Apiezon L (25%) on Chromosorb W at 190°. The first peak was due to 2,2'-dimethoxybiphenyl, m.p. 154—155°, the second to 4-chloro-2'-methoxybiphenyl, m.p. 50—51° (lit.,^{5b} m.p. 53°), and the third to 4,4'-dichlorobiphenyl, m.p. 147—148° (lit.,¹⁸ m.p. 148°).

4-Chloro-3'-methoxybiphenyl.—The reaction mixture from m-iodoanisole (1.0 g.), p-chloroiodobenzene (1 g.), and copper-bronze (4 g.) in sulpholan (5 ml.) was dissolved in boiling acetone (4×50 ml.) and the acetone extract concentrated. 4,4'-Dichlorobiphenyl separated and, after recrystallisation from methanol, gave white crystals (15 mg.), m.p. 146—147°. The acetone mother liquors were concentrated and resolved by g.l.c. to give 4-chloro-3'-methoxybiphenyl, m.p. 32° (lit.,^{5b} m.p. 36—37°), and 3,3'-dimethoxybiphenyl, m.p. 32°. The i.r. spectrum of the latter was identical with that of the product obtained from the reaction of o- and m-iodoanisole above.

4-Chloro-4'-methoxybiphenyl.—The products from the reaction of p-iodoanisole and p-chloroiodobenzene were resolved by g.l.c. The first peak was due to 4,4-dichlorobiphenyl, m.p. 148°, the second to 4-chloro-4'-methoxybiphenyl, m.p. 115—116° (lit.,⁵⁵ m.p. 116°), and the third to 4,4'-dimethoxybiphenyl, m.p. 174°.

Diazonium Tetrafluoroborates.—These were freshly prepared for each reaction by Roe's method.¹⁹ They were washed with ice-cold 5% aqueous sodium tetrafluoroborate, ice-cold methanol, and ice-cold ether, and were stored in a desiccator before use. *p*-Methoxybenzenediazonium tetrafluoroborate could not be obtained pure in this way and was prepared by the diazotisation of a solution of *p*-anisidine in 48% fluoroboric acid.²⁰ The m.p.s of the salts were: *p*-nitro-, 168° (decomp.); *p*-methyl-, 108—109° (decomp.); *p*-methoxy-, 148—150° (decomp.); *m*-methoxy-, 93° (decomp.); *p*-chloro-, 132—133° (decomp.).

Decomposition of m-Methoxybenzenediazonium Tetrafluoroborate in Nitrobenzene: 3-Methoxy-4'-nitrobiphenyl.—m-Methoxybenzenediazonium tetrafluoroborate (4·4 g.) was decomposed in nitrobenzene (250 ml.) in the presence of pyridine (1·6 g.) at 60° for 8 hr. with stirring. The excess of nitrobenzene was distilled and the residue was chromatographed on alumina (50 g.). Elution with benzene gave the mixture of the isomeric products which were resolved by g.l.c. on a 2 ft. $\times \frac{1}{4}$ in. column packed with Apiezon N (20%) on Chromosorb W at 190° and a helium flow rate of 120 ml./min. The first two peaks corresponded to 2- and 3-nitro-3'-methoxybiphenyl. The third peak was due to 3-methoxy-4'-nitrobiphenyl, m.p. 88—89° (lit.,^{5e} m.p. 90—91°), identical with the sample prepared by the Ullmann reaction.

Decomposition of p-Nitrobenzenediazonium Tetrafluoro-¹⁹ A. Roe, Org. Reactions, 1949, 5, 203.

²⁰ J. Elks and D. H. Hey, J. Chem. Soc., 1943, 441.

borate in Anisole.-p-Nitrobenzenediazonium tetrafluoroborate (4.6 g.) was decomposed in anisole (200 ml.) in the presence of pyridine (1.6 g.) at 60° for 8 hr. with stirring. Excess of anisole was distilled off and the residue was chromatographed on alumina (50 g.). Elution with light petroleum (b.p. $40-60^{\circ}$)-benzene (l: l v/v) gave the mixture of isomers which was resolved by g.l.c. on the above column at 210°. The first peak was due to 2-methoxy-4'nitrobiphenyl, m.p. $50-51^{\circ}$ undepressed on admixture with the product from the Ullmann reaction. The i.r., n.m.r., and mass spectra were also identical to those of the authentic sample. The second peak was due to 3-methoxy-4'-nitrobiphenyl, m.p. 88-89° undepressed on admixture with an authentic sample. The third was due to 4-methoxy-4'-nitrobiphenyl, m.p. and mixed m.p. 107-108°, identical in i.r. and n.m.r. spectrum to the authentic sample.

Decomposition of p-Methylbenzenediazonium Tetrafluoroborate in Anisole.--p-Methylbenzenediazonium tetrafluoroborate (4.12 g.) was decomposed in anisole (200 ml.) and pyridine (1.6 g.) and the mixture worked up as above. G.l.c. on a 4 ft. $\times \frac{1}{4}$ in. column packed with Apiezon L (25%) on Chromosorb W at 180° and a helium flow rate of 60 ml./min. showed the presence of four products. The first, retention time 9 min., was 4-methyldiphenyl ether, b.p. $117^{\circ}/3$ mm., whose i.r. spectrum was identical to that of the authentic sample. The second, retention time 22 min., was 2-methoxy-4'-methylbiphenyl, m.p. 79-80°. The third, retention time 37 min., was 3-methoxy-4'-methylbiphenyl, b.p. 100°/1 mm., whose i.r. and mass spectra were identical with those of the sample prepared by the Ullmann reaction. The fourth, retention time 41 min., was 4-methoxy-4'-methylbiphenyl, m.p. 109-110°.

Decomposition of m-Methoxybenzenediazonium Tetrafluoroborate in Anisole.—m-Methoxybenzenediazonium tetrafluoroborate was decomposed as above and the products were resolved as for the p-tolylation. Four products were obtained which were collected and shown to be identical with 3-methoxydiphenyl ether, b.p. $140^{\circ}/3$ mm., 2,3'-dimethoxybiphenyl, m.p. 39— 40° , 3,3'-dimethoxybiphenyl, m.p. 32° , and 3,3'-dimethoxybiphenyl, m.p. 57° .

General Procedure for Arylations.—This has been described.¹² The reactions were carried out in triplicate and the products were analysed quantitatively by g.l.c. by use of the internal standard technique.²¹ Each run was analysed in triplicate and the average results recorded.

p-Nitrophenylation of Anisole.—A solution of p-nitrobenzenediazonium tetrafluoroborate (0.237 g., 0.001 mole), anisole (22 ml., 0.2 mole), and pyridine (0.079 g., 0.001 mole) in sulpholan (10 ml.) was stirred at room temperature for 1 hr., then at 60° for 7 hr. under dry oxygen-free nitrogen. Analysis was on a 2 ft. $\times \frac{1}{4}$ in. column packed with Apiezon L (20%) on Chromosorb W (60—80 mesh) at a programmed temperature of 100—200° and a helium flow rate of 30 ml./ min., with 2-nitrobiphenyl as internal standard. The isomer ratio of x-methoxy-4'-nitrobiphenyl was: 2-methoxy-, 69.2 \pm 0.3; 3-methoxy-, 14.5 \pm 0.2; 4-methoxy-, 16.3 \pm 0.3%. The average overall yield was 81 \pm 0.1%.

p-Tolylation of Anisole.—Analysis was on a 6 ft. \times 1 in. column packed with Apiezon L (25%) in Gas Chrom P at 190° and a helium flow rate of 67 ml./min. with 2-bromobiphenyl as internal standard. The isomer ratio of xmethoxy-4'-methylbiphenyl was: 2-methoxy-, $58\cdot 2 \pm 0.4$; 3-methoxy-, $24\cdot 2 \pm 0.6$; 4-methoxy-, $17\cdot 6 \pm 0.4\%$. The ²¹ T. C. Chang and C. Karr, jun., Analyt. Chim. Acta, 1959, 21, 474. average overall yield was $23.5 \pm 1.7\%$. In addition, 4-methyldiphenyl ether was obtained in 5.5% yield.

p-Methoxyphenylation of Anisole.—Analysis was on a 6 ft. \times 1 in. column packed with Apiezon L (25%) on Gas Chrom P (100—120 mesh) at 200° and a helium flow rate of 67 ml./min., with 2-bromobiphenyl as internal standard. The isomer ratio of x-methoxy-4'-methoxybiphenyl: 2-methoxy-, 63.0 \pm 1.2; 3-methoxy-, 18.0 \pm 1.0; 4-methoxy-, 19.0 \pm 1.1%. The average overall yield was $34.2 \pm 2.4\%$.

m-Methoxyphenylation of Anisole.—Analysis was on a 6 ft. $\times \frac{1}{4}$ in. column of Apiezon L (20%) on Chromosorb W (60—80 mesh) at 180° and a helium flow rate of 70 ml./min. with 2-bromobiphenyl as internal standard. The isomer ratio of x,3'-dimethoxybiphenyl was: 2-, 52.7 \pm 0.6; 3-, 16.7 \pm 0.1; 4-, 30.5 \pm 0.7%. The average overall yield was 29.0 \pm 2.7%. 3-Methoxydiphenyl ether was also obtained in 7% yield.

p-Chlorophenylation of Anisole.—Analysis was as for the m-methoxyphenylations but at 170°. The isomer ratio of x-methoxy-4'-chloroanisole: 2-methoxy-, 64.7 ± 0.6 ; 3-methoxy-, 19.4 ± 0.3 ; 4-methoxy-, $15.9 \pm 0.8\%$. The average overall yield was $41 \pm 1\%$.

Determination of Total Rate Ratios.—Competitive reactions. The reactions were carried out as for the non-competitive runs except that a mixture of substrates in various molar proportions was used and varying amounts of pyridine. The results are summarised in Table 4.

TABLE 4

Total rate ratio in the arylation of anisole at 60°

		[Salt]:	Molar	
	[Anisole]:	Total	equiv. of	MeO _H K-
Radical	[Benzene]	substrate]	pyridine	$(X \cdot C_6 H_4 \cdot)^{a}$
p-NO ₂ ·C ₆ H ₄ ·	1:1	1:400	1	2.80
p-NO, C, H4	1:1	1:400	3	2.80
p-NO [•] C ₆ H [•]	4:1	1:500	1	2.87
p-NO2 CBH4	1:4	1:500	1	2.87
p-Me·C ₆ H ₄ ·	1:1	1:400	1	1.06
p-Me·C ₆ H₄·	1:1	1:400	3	1.17
p-Me•C ₆ H₄•	4:1	1:500	1	1.00
p-Me·C ₆ H ₄ ·	1:4	1:500	1	1.09
p-Cl·C ₆ H ₄ ·	1:1	1:400	1	2.22
p-Cl·C ₆ H ₄ ·	1:1	1:400	3	2.29
p-Cl·C ₆ H ₄ ·	4:1	1:500	1	$2 \cdot 20$
p-Cl·C ₆ H ₄ ·	1:4	1:500	1	2.32
m-MeO·C ₆ H ₄ ·	1:1	1:400	1	1.91
p-MeO·C ₆ H ₄ ·	1:1	1:400	1	1.97
p-MeO·C ₆ H ₄ · ¹) 1:1	1:400	1	1.95
p-MeO C ₆ H ₄	1:1	1:400	3	1.61
p-MeO·C ₆ H ₄ ·	1:1	1:400	0	3.38
p-MeO·C ₆ H₄·	3:1	1:400	1	1.68
p-MeO·C ₆ H ₄ ·	3:1	1:400	3	1.70
p-MeO·C ₆ H ₄ ·	4:1	1:500	1	1.64
p-MeO•C ₆ H₄•	4:1	1:500	3	1.64
p-MeO·C ₆ H ₄ ·	1:3	1:400	1	2.37

^a Statistical correction applied as required. ^b Acetonitrile used as the solvent instead of sulpholan.

DISCUSSION

The isomer ratios obtained in the arylation of anisole are collected in Table 5. No pattern is evident other than the usual predominance of attack at the orthoposition, unlike the situations with nitrobenzene⁶ and pyridine^{8,9} as substrates. It appears from this and other points of view that anisole is not a good substrate for the evaluation of radical polarities. Differences

J. Chem. Soc. (B), 1969

between the present data and those in the literature could be ascribed to differences in temperature, analytical techniques, and reagents.

In the p-tolylation of anisole some 4-methyldiphenyl ether was formed. A similarly low yield of 3-methoxydiphenyl ether was obtained in the *m*-methoxyphenylation of anisole. Though radical pathways can be agreement with the theory of polarised radicals. Both the *p*-tolyl and the *p*-methoxyphenyl radicals are more nucleophilic than the phenyl radical, as had been shown earlier with pyridine as the substrate. A plot of $\log {}^{\text{MeO}}_{\text{H}}K$ against σ (Figure) or σ^+ (but not σ^0) gave a reasonably good straight line with $\rho = 2 \cdot 1$. The point for the *p*-tolyl radical was well below that line,

TABLE	5
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Isomer and total rate ratios in the arylation of anisole at 60°						
Radical	C ₆ H₅∙	p-NO ₂ ·C ₆ H ₄ ·	p-Cl·C ₆ H ₄ ·	<i>m</i> -MeO·C ₆ H ₄ ·	p-MeO·C ₆ H ₄ ·	p-Me•C ₆ H₄•
ortho (%)	59.2	69 ·0	64.7	$52 \cdot 8$	63.0	58.2
meta (%)	16.8	14.6	19.6	16.7	18.0	$24 \cdot 2$
para (%)	24.0	16.4	15.9	30.5	19.0	17.6
MeO _H K	1.91	2.80	$2 \cdot 22$	1.91	1.64	1.17

envisaged to account for the formation of these compounds it seems more likely that they arise by a cationic attack (1) upon the methoxyl group. Thus it appears

$$Ar^{+} + :O^{-}C_{6}H_{5} \xrightarrow{Me} Ar^{-}O^{+}-C_{6}H_{5} \xrightarrow{BF_{4}^{-}} Ar^{-}O^{-}C_{6}H_{5} + MeF + BF_{3} \quad (1)$$

that in these cases a small amount of uncatalysed thermal decomposition is taking place together with the catalysed homolytic cleavage. No copious amount of BF3 were observed as was the case with the uncatalysed thermolyses.¹³ No diphenyl ether were observed with the other radicals. The formation of these diphenyl ethers was not significant in the competitive reactions since a very large excess of the mixture of substrates was used and no correction was necessary within the limits of accuracy of the experiment. The p-methoxybenzenediazonium salt also exhibited a tendency to undergo heterolytic fission to the cation in the competitive reactions even in the presence of one equivalent of pyridine. This could be suppressed by the addition of three equivalents of pyridine per mole of diazonium salt or by the use of a greater proportion of anisole over benzene. As the relative amount of anisole was increased the value of ${}^{MeO}_{H}K$ fell, indicating that this effect was not due to a selective solvation of the cation by the anisole (had this been the case $MeO_{\mathbf{H}}K$ should have increased with increasing proportions of anisole) but rather to a change of mechanism. The low value of $^{MeO}_{H}K = 1.64$ was attained either by the addition of three equivalents of pyridine or by increasing the proportion of anisole. It appears as though both pyridine and anisole function as bases and shift the equilibrium (2) to the right, thus ensuring homolytic fission of the diazo compound. The rate ratio of 1.64

$$p$$
-MeO·C₆H₄N₂⁺ + :B $\Longrightarrow p$ -MeO·C₆H₄-N=N-B⁺ (2)

is thus that for the free radical p-methoxyphenylation of anisole, and the value of 3.38 would be that for the substitution by the p-methoxyphenyl cation or biradical cation.¹⁵

The total rate ratios (Table 5) are in qualitative

however, and a repetition of the p-tolylation competitive runs under a variety of conditions failed to lead to any improvement. This suggests that the p-tolyl radical is more nucleophilic than would be expected on the basis of σ_{p} .Me. A similar observation was made in the arylations of pyridine. We cannot yet explain this. There is a further point concerning total rate ratios On the basis of σ_{m} .MeO = 0.115 one would have expected



Relation of $\log {}^{MeO}_{H}K(X \cdot C_{g}H_{4})$ to σ_{X} for the arylation of anisole with $X \cdot C_{g}H_{4}N_{2}^{+}BF_{4}^{-}$ and $C_{5}H_{5}N$ where X is: A, p-NO₂; B, p-Cl; C, *m*-MeO; D, H; E, p-MeO; and F, p-Me

 ${}^{\text{MeO}}_{\text{H}}K(m\text{-MeO}\cdot\text{C}_{6}\text{H}_{4}) = 2\cdot01$. In fact it was found (reproducibly) to be no more electrophilic than phenyl itself (${}^{\text{MeO}}_{\text{H}}K = 1\cdot91$). Though the difference is small it is worth trying to explain this. Taft, Fox, and Lewis²² observed that in a number of instances a *m*-methoxy-substituent enhanced the reactivity in radical reactions by about 0·3 kcal./mole and attributed this to an enhancement of the resonance effect by the *meta* substituent as shown in (3). σ_m Constants are

derived by looking at the effect of the substituent along a *filled* σ -orbital in the *meta*-position. In the *m*-meth-²² R. W. Taft, I. R. Fox, and I. C. Lewis, *J. Amer. Chem. Soc.*, 1961, **83**, 3349.

TABLE	6
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Partial rate factors for the arylation of anisole at 60°

Radical	Ph•	p-NO₂C ₆ H₄·	p-ClC ₆ H ₄ ·	m-MeOC ₆ H ₄ ·	p-MeOC ₆ H ₄ ·	p-MeC ₆ H ₄
F_{o}	3.38	5.7	4 ·30	2.99	3.09	$2 \cdot 05$
F_m	0.96	1.2	1.29	0.98	1.00	0.89
F_p	2.72	$2 \cdot 6$	2.09	3.51	1.64	1.12

oxyphenyl radical (Ia) this orbital is only partially filled, and one can visualise a concerted uncoupling of the π -electrons occurring, with one of the π -electrons



dropping into the partially vacant σ -orbital to give (Ib) for which a number of contributing structures could be written. This is similar to the suggestion made to account for the properties of aryl cations.^{15,23,24} (Ib) would behave as a nucleophile and to the extent that it was formed it would decrease the net effective observed electrophilicity of the attacking species to a small extent, which is what is observed. If this suggestion has any merit, it would imply that the effect of the substituent upon the polarity of the radical will depend upon its effect on the permanent polarisation of the radical and not of a parent species.

The partial rate factors for the arylation of anisole are in Table 6.

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²³ R. W. Taft, J. Amer. Chem. Soc., 1961, 83, 3350.

²⁴ R. A. Abramovitch and J. G. Saha, *Canad. J. Chem.*, 1965, **43**, 3269.