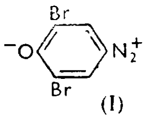
# 866. *A Further Study of the Thermal Decomposition of 3 : 5-Dibromobenzene 1 : 4-Diazo-oxide.*

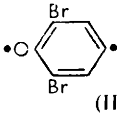
By M. J. S. DEWAR and A. N. JAMES.

3 : 5-Dibromobenzene 1 : 4-diazo-oxide has been decomposed in a variety of aromatic solvents and the total relative rate factors for reaction of the intermediate with the solvent have been determined. The variation of these factors with solvent structure confirms the earlier deduction [1] that the intermediate is a diradical.

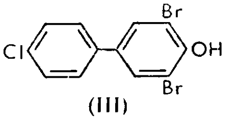
IN a previous paper [1] we deduced that the first step in the decomposition of 3 : 5-dibromobenzene 1 : 4-diazo-oxide (I) in chlorobenzene was elimination of nitrogen, giving rise to the diradical (II). It was argued that the radical centre *para* to oxygen should have the same order of reactivity as that in phenyl monoradical, and the formation of polymers with molecules of solvent incorporated was ascribed to radical-substitution of the solvent through this reactive centre. We have now found that similar reactions take place in *o*- and *p*-dichlorobenzene, in bromobenzene, and in nitrobenzene, giving rise to polymers of analogous structure.



(I)



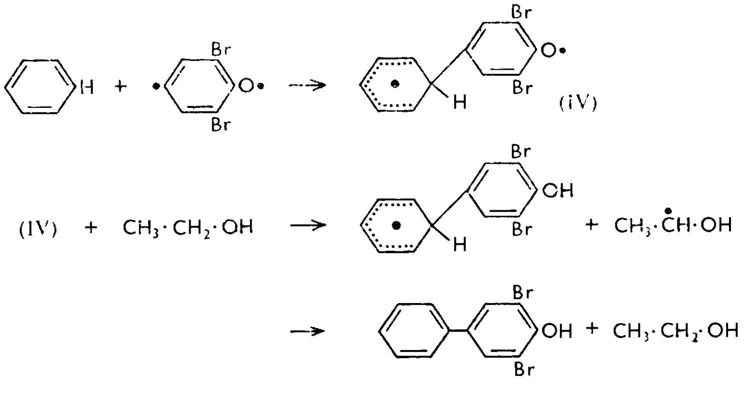
(II)



(III)

We also reported [1] that the decomposition of the diazo-oxide in chlorobenzene gave small amounts of diphenyl derivatives, the compound (III) being isolated in a pure state. We have now found that this type of reaction predominates in benzene, fluorobenzene, anisole, *NN*-dimethylaniline, or benzonitrile, giving rise to 3 : 5-dibromo-4-hydroxydiphenyl derivatives in fair yields.

This second mode of decomposition could be made to predominate in all cases, by adding 1% of ethanol; the ethanol probably acted as a hydrogen-transfer catalyst by the path shown in the reaction scheme. The first step of this mechanism involves radical-substitution of the aromatic solvent by a substituted phenyl radical; it seemed to us that this mechanism could be confirmed by comparing the total relative rate factors for attack on different solvents with those measured by Hey and his collaborators [2] for the analogous reaction of phenyl radicals.



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[1] Dewar and James, *J.*, 1958, 917.

[2] Hey *et al.*, *J.*, 1934, 1727; 1952, 1974, 2094; 1953, 44; 1954, 794, 1425, 3352; 1955, 6, 1425; 1956, 1475.

The measurements were carried out by the competitive method, using mixtures of the various substituted benzenes with benzene itself, in presence of ethanol. The reactions seemed to proceed particularly well under these conditions; the yields of mixed hydroxydiphenyls being over 85% in all but one case. The proportions of diphenyls were determined by elementary analysis.

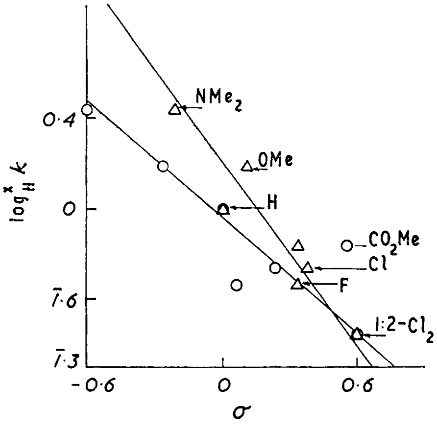
Nitrobenzene proved exceptional. Decomposition of the diazo-oxide in a mixture of benzene and nitrobenzene gave a rather low yield of 3 : 5-dibromo-4-hydroxydiphenyl, and a polymer which appeared to consist of bromodiphenylyloxy- and dibromophenoxy-units. Neither product contained nitrogen. On the other hand nitrosobenzene was found in significant quantities, and polarography indicated the presence of 2 : 6-dibromobenzoquinone. It is possible that reaction of the diradical (II) with nitrobenzene gives

[redacted]

It is also clear that the diradical (II) shows significant electrophilic character, just as do the relatively electronegative radicals derived from chlorobenzoyl and nitrobenzoyl peroxide.[3] This is also indicated in the Figure which shows Hammett plots of the total relative rate factors for the diazo-oxide (I) against σ-constants for the substituents. Since the orientations of the products are not known, plots are shown for *meta* and *para* σ-constants. These suggest that methyl benzoate is probably *meta*-substituted largely, in accordance with the apparently marked electrophilic nature of the diradical (II).

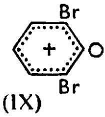
TABLE 1. *Total relative rate factors for reaction of diradical* (I) *and phenyl radicals with various benzene derivatives.*

| Solvent | $^{\mathrm{X}}_{\mathrm{H}}k$(I) | $^{\mathrm{X}}_{\mathrm{H}}k$(Phenyl) |
|---|---|---|
| *NN*-Dimethylaniline ... | 2·8 | — |
| Pyridine ................. | 2·6 | 1·04 |
| Anisole ..................... | 1·6 | 2·50 |
| Fluorobenzene ........... | 0·46 | 1·35 |
| Me benzoate ........... | 0·78 | — |
| Chlorobenzene ........... | 0·54 | 1·44 |
| *o*-Dichlorobenzene ...... | 0·28 | — |



*Plots of* log $^{\mathrm{X}}_{\mathrm{H}}k$ *against* σ *for* para- (○) *and* meta-*substitution* (△).

This electrophilic character can be ascribed to a polarisation of the π-electrons by the electronegative oxygen atom, the structure approximating to (IX).



(IX)

Further evidence for the electrophilic nature of the diazo-oxide (I) is provided by the partial rate factors for *ortho-*, *meta-*, and *para*-substitution in chlorobenzene. The proportions of isomers in the diphenyl fraction were determined by ultraviolet spectrophotometry,[4] and the partial rate factors were then calculated by using the known overall reactivity of chlorobenzene relative to benzene (Table 1). Table 2 shows the partial rate factors for reaction of chlorobenzene with the diazo-oxide (I), with phenyl radicals, and with acetyl nitrate.[5]

[redacted]

## EXPERIMENTAL

*Materials.*—3 : 5-Dibromobenzene-1 : 4-diazo-oxide was prepared in quantities of about 10 g. by Böhmer's procedure [6] and dried in a vacuum over phosphoric oxide for 2 days. The compound should be handled carefully and in small quantities since it is dangerously explosive; in an earlier investigation considerable damage was caused by the detonation of 70 g. of the material on gentle rubbing. Chlorobenzene was washed with concentrated sulphuric acid and water, dried ($CaCl_2$), and fractionated from phosphoric oxide. *o*-Dichlorobenzene and fluorobenzene were fractionated from phosphoric oxide. Bromobenzene was fractionated under reduced pressure from phosphoric oxide. Nitrobenzene was distilled and then purified by partial freezing. *NN*-Dimethylaniline (" AnalaR ") and *p*-dichlorobenzene (" purified " grade) were redistilled. Benzonitrile was washed with aqueous potassium carbonate, dried ($CaCl_2$; $P_2O_5$), and distilled. Anisole was dried ($CaCl_2$), then distilled in a vacuum. Decalin was washed with dilute sulphuric acid, aqueous alkali, and water. After drying ($CaSO_4$) it was fractionated under reduced pressure. Carbon tetrachloride was boiled under reflux with 5% sodium hydroxide solution, washed with water, dried ($CaCl_2$), and distilled. Pyridine, after several days over potassium hydroxide, was distilled from fresh potassium hydroxide. Methyl benzoate was prepared in the usual way from " AnalaR " benzoic acid, dried ($CaCl_2$), and distilled. Ethanol was dried with magnesium and distilled. Benzene (crystallisable grade) was dried (Na wire) and distilled.

*Decompositions in Pure Solvents.*—These were carried out by heating weighed portions (2—4 g.) of diazo-oxide (I) in pure solvents (250 c.c.) at 80° (thermostat) with stirring.

The diazo-oxide (3·00 g., 0·0108 mole) in *o*-dichlorobenzene gave in 2 hr. much tar and polymer (0·9 g.) [Found: C, 47·0; H, 2·2; Br, 25·2; Cl, 23·8. Calc. for $(C_{12}H_5OCl_2Br)_n$: C, 45·6; H, 1·6; Br, 25·3; Cl, 22·5%].

The diazo-oxide (2·95 g.) in *p*-dichlorobenzene gave in 2 hr. a little tar and polymer (1·3 g.) (Found: C, 46·3; H, 2·0; Br, 30·5; Cl, 13·6. Calc. for copolymer of $C_{12}H_5OClBr$ (85%) and $C_6H_2OBr_2$ (15%): C, 43·6; H, 1·6; Br, 30·1; Cl, 15·2%).

The diazo-oxide (1·80 g.) in bromobenzene gave polymer (0·95 g.) [Found: C, 44·9; H, 2·3; Br, 48·2. Calc. for $(C_{12}H_6OBr)_n$: C, 44·2; H, 1·8; Br, 49·9%]. Some tar (0·25 g.) and phenolic material (0·35 g.) were also formed.

The diazo-oxide (2·85 g.) in nitrobenzene gave in 2 hr. polymer (0·6 g.) (Found: C, 41·4; H, 2·2; O, 11·4; N, 1·8. Calc. for 1 : 1 copolymer of $C_{12}H_6O_3NBr$ and $C_6H_2OBr_2$: C, 40·0; H, 1·6; O, 11·8; N, 2·5%). There were also isolated tarry phenols (1·20 g.) from which 2 : 4 : 6-tribromophenol (0·2 g.) was obtained by steam-distillation and converted into the methyl ether, m. p. and mixed m. p. 86°.

The diazo-oxide (0·85 g.) in fluorobenzene gave in 1 hr. a crystalline phenol (0·9 g., 70%). Repeated recrystallisation from light petroleum (b. p. 60—80°)–chloroform gave 3 : *5-dibromo-4'-fluoro-4-hydroxydiphenyl* as needles, m. p. 150—151° (Found: C, 41·7; H, 2·0. $C_{12}H_7OBr_2F$ requires C, 41·7; H, 2·3%). 4-Fluoro-4'-hydroxydiphenyl, prepared from the amino-compound by the method employed for 4-chloro-4'-hydroxydiphenyl, crystallised from chloroform in needles, m. p. 167—168° (lit.,[7] m. p. 167—168°); it (0·4 g.) was converted into the above dibromo-derivative by bromine (0·68 g.) in carbon disulphide (10 c.c.), and this crystallised as above in needles, m. p. and mixed m. p. 150—151°. The monomethyl ether crystallised from light petroleum (b. p. 40°) in needles, m. p. 107—108°.

The diazo-oxide (2·25 g.) in *NN*-dimethylaniline gave in 2 hr. a deep red solution which was extracted with 5N-sodium hydroxide. The alkaline extract on acidification (pH 5·0) deposited a dark phenolic mixture (2·0 g., 70%). This mixture was methylated (diazomethane) and the product converted into its picrate (impure), needles, m. p. 191—192° (decomp.) (from alcohol) (Found: C, 41·0; H, 2·9; N, 9·1; Br, 26·0. Calc. for $C_{15}H_{15}ONBr_2,C_6H_2ON_3$ : C, 41·0; H, 3·1; N, 9·0; Br, 24·0%). The base, liberated by concentrated aqueous ammonia, crystallised from alcohol in rosettes (still impure), m. p. 71—72° (Found: C, 46·5; H, 4·0; N, 3·6; Br, 42·3. Calc. for $C_{15}H_{15}ONBr_2$: C, 46·7; H, 3·9; N, 3·6; Br, 41·6%).

The diazo-oxide (2·90 g.) in benzonitrile gave in 2 hr. a mixture of phenols (2·8 g., 80%) from which two isomers, 3 : *5-dibromo-*x'*-cyano-4-hydroxydiphenyl*, were obtained. One crystallised from benzene in needles, m. p. 230—231° (Found: C, 44·7; H, 2·2; N, 3·9; Br, 45·2;

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[6] Bohmer, *J. prakt. Chem.*, 1881, **24**, 453.

[7] Fleishman and Roe, *J. Amer. Chem. Soc.*, 1947, **69**, 509.

$C_{13}H_7ONBr_2$ requires C, 44·2; H, 2·2; N, 3·9; Br, 45·2%), the other from alcohol in needles, m. p. 182—184° (Found: C, 43·9; H, 2·2; N, 4·0; Br, 44·9%).

The diazo-oxide (2·85 g.) in anisole gave in 3 hr. a mixture of phenols (3·45 g., 95%) from which 3 : 5-dibromo-4-hydroxy-4′-methoxydiphenyl was obtained by repeated recrystallisation from light petroleum (b. p. 60—80°) as pale brown needles, m. p. 128—129° (Found: C, 43·8; H, 3·1; Br, 43·6; OMe, 8·6. Calc. for $C_{13}H_{10}O_2Br_2$: C, 43·6; H, 2·8; Br, 44·46; OMe, 8·7%). Boiling the product (0·7 g.) with hydriodic acid in acetic acid gave the diphenyl (0·1 g.), m. p. 272—274° (from benzene) (lit.,[8] m. p. 274—275°).

The diazo-oxide (2·25 g.) in decalin gave in 24 hr. 2 : 6-dibromophenol (0·75 g.) which crystallised from hot water in needles, m. p. and mixed m. p. 55—56°. Polymer (0·5 g.) was also obtained [Found: C, 59·5; H, 5·7; Br, 27·7. Calc. for a copolymer of $C_{10}H_{16}$ (66%) and $C_6H_2OBr_2$ (34%): C, 59·4; H, 6·4; Br, 31·1%].

The diazo-oxide (2·10 g.) in carbon tetrachloride gave in 18 hr. a red solution from which was obtained a polymer (0·35 g.) (Found: C, 31·9; H, 1·4; Br, 51·1; Cl, 9·8. Calc. for a 1 : 1 copolymer of $C_6H_2OBr_2$ and $C_6H_2OClBr$: C, 31·6; H, 0·9; Br, 52·6; Cl, 7·8%). There was also obtained an ether-soluble solid (1·1 g.) which did not crystallise.

*Competitive Experiments.*—These were carried out by heating the diazo-oxide (about 3 g.) in an equimolecular mixture of benzene and a second solvent containing ethanol (1% v/v) at 80° (thermostat) with stirring. The phenolic product was then extracted with aqueous sodium hydroxide, weighed, and in several cases methylated (diazomethane). The ethers were purified by passage in benzene down a column of alumina with about 5% loss of product. Independent experiments showed that the recovery of the ethers was almost quantitative.

*Chlorobenzene.* The diazo-oxide (2·75 g.) was decomposed in 5 hr. to a phenolic mixture (2·80 g., 87%), methylation of which (1·05 g.) gave pale yellow crystals (1·10 g.) [Found: C, 44·0; H, 2·7; Br, 45·0; Cl, 3·4. Calc. for $C_{13}H_9OClBr_2$ (36%) and $C_{13}H_{10}OBr_2$ (64%): C, 44·0; H, 2·9; Br, 44·8; Cl, 3·6%].

o-*Dichlorobenzene.* The diazo-oxide (3·00 g.) was decomposed in 4½ hr. to an orange-brown phenolic mixture (3·35 g., 95%), which (1·35 g.) gave a pale-orange crystalline methyl ether (1·25 g.) [Found: C, 43·7; H, 2·9; Br, 42·9; Cl, 4·4. Calc. for $C_{13}H_8OCl_2Br_2$ (22%) and $C_{13}H_{10}OBr_2$ (78%): C, 43·7; H, 2·7; Br, 44·8; Cl, 4·4%].

*Fluorobenzene.* The diazo-oxide (3·00 g.) was decomposed in 6 hr. to almost white, crystalline phenols (3·25 g., 86%) which yielded on methylation a crystalline mixture of methyl ethers (3·15 g.) [Found: C, 44·4; H, 2·6; Br, 46·9; F, 1·7. Calc. for $C_{13}H_9OBr_2F$ (31·4%) and $C_{13}H_{10}OBr_2$ (68·5%): C, 44·8; H, 2·8; Br, 46·1; F, 1·7%].

*Anisole.* The diazo-oxide (2·00 g.) was decomposed in 4½ hr. to a pale yellow crystalline phenolic mixture (2·30 g., 93%), which (0·75 g.) was methylated to a pale yellow oil (0·75 g.) [Found: C, 45·0; H, 3·4; Br, 43·9; OMe, 13·9. Calc. for $C_{14}H_{12}O_2Br_2$ (39%) and $C_{13}H_{10}OBr_2$ (61%): C, 45·3; H, 3·1; Br, 44·4; OMe, 13·8%].

NN-*Dimethylaniline.* The diazo-oxide (2·95 g.) decomposed in 2 hr., giving a deep red solution which on extraction with alkali and acidification (pH 5) deposited a dark brown crystalline phenolic mixture (3·15 g., 87%). Methylation of this (0·85 g.) gave a brown liquid (0·80 g.) [Found: C, 42·8; H, 3·2; N, 2·2; Br, 47·7. Calc. for $C_{15}H_{15}ONBr_2$ (61%), $C_{13}H_{10}OBr_2$ (22%), and $C_7H_5OBr_3$ (17%): C, 43·0; H, 3·3; N, 2·3; Br, 47·0%].

*Pyridine.* The diazo-oxide (2·1 g.) gave in 1½ hr. a very dark red solution. After removal of the rest of the solvent under reduced pressure, the black residue was dissolved in ether and extracted with alkali, giving a dark phenolic mixture (2·30 g., 86%), methylated to a brown liquid (2·15 g.) [Found: C, 43·1; H, 3·1; N, 2·9; Br. 47·4. Calc. for $C_{12}H_9ONBr_2$ (72%) and $C_{13}H_{10}OBr_2$ (28%): C, 43·0; H, 2·8; N, 2·9; Br, 47·1%].

*Methyl benzoate.* The diazo-oxide (3·00 g.) was decomposed in 5 hr. to a dark red solution from which a crystalline phenolic mixture (3·80 g., 95%) was isolated and converted into mixed methyl ethers (3·65 g.) [Found: C, 43·4; H, 2·9; Br, 45·0. Calc. for $C_{14}H_{10}O_3Br$ (44%) and $C_{13}H_{10}OBr$ (56%): C, 44·4; H, 2·7; Br, 44·5%]. The product (1·533 g.) with alcoholic 0·5N-potassium hydroxide gave a non-acidic component (0·806 g., 56%) which on one recrystallisation from light petroleum (b. p. 60—80°) yielded pale brown needles of 3 : 5-dibromo-4-hydroxydiphenyl, m. p. and mixed m. p. 95—96°. The acidic component (0·755 g., 44%) was dissolved in alcohol and titrated to phenolphthalein (Found: equiv., 393. Calc. for $C_{14}H_{10}O_3Br_2$: equiv., 386).

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[8] Hirsh, *Ber.*, 1889, **22**, 235.

*Nitrobenzene*. The diazo-oxide (3·00 g.) decomposed in 5 hr., giving a dark red solution, from which a phenolic mixture (0·95 g., 27%) was obtained (Found: C, 43·6; H, 3·0; Br, 47·7. Calc. for $C_{12}H_8OBr_2$: C, 42·2; H, 2·5; Br, 48·6%). The extracted solution was dried ($CaCl_2$) and distilled under reduced pressure. When the nitrobenzene began to distil (~120°/14 mm.) the distillate became green. This distillate was compared spectroscopically with a solution of nitrosobenzene in nitrobenzene (413 mg./l.) and shown to have an identical band at 745 mμ. After the solution had been evaporated to about 5 c.c. it was poured into stirred methanol, to yield an orange polymer (1·25 g., 50%) [Found: C, 51·3; H, 3·5; Br, 38·1. Calc. for $C_6H_2OBr_2$ (20%) and $C_{12}H_7OBr$ (80%): C, 52·2; H, 2·4; Br, 38·7%]. The filtrate after removal of polymer and phenolic products was concentrated under reduced pressure to about 2 c.c. A filtered solution of this residue (0·85 g.) in alcohol (50 c.c.) and phosphate buffer (50 c.c.) (final pH 7·45) was examined polarographically. It showed a half-wave at −0·05v with reference to a calomel electrode. The wave was slightly masked by condenser current. However, variation of the concentration of the solution showed this half-wave to be characteristic. Similar behaviour was shown by solutions of 2 : 6-dibromobenzoquinone. The half-wave potentials obtained for solutions of $2 \times 10^{-4}$, $5 \times 10^{-4}$, and $2 \times 10^{-3}$ mole/l. were −0·04, −0·07, and −0·12 v respectively.

*Partial Rate Factors for Chlorobenzene*.—Decomposition of the diazo-oxide (3·00 g.) in chlorobenzene (250 c.c.) containing ethanol (2·5 c.c.) in 3 hr. gave a phenolic fraction (3·90 g., 96%) which was methylated to a pale yellow oily mixture of isomeric 3 : 5-dibromo-*x*′-chloromethoxydiphenyls (3·85 g.). It was analysed spectrophotometrically by the method of Dewar and Urch[4] (Found: 2′, 60·0%; 4′, 40·0%). The preparation of the necessary reference compounds is described below. All spectra were measured with a Unicam S.P. 1500 spectrophotometer. The 2′ : 4′ ratio is unlikely to be in error by more than 1%.

3 : 5-*Dibromo*-4′-*chloro*-4-*methoxydiphenyl*.—The following procedure gives a better yield than our previous method.[1] 4-Chloro-4′-nitrodiphenyl[9] crystallised from acetic acid in yellow needles, m. p. 141·5—142·5°, not altered by repeated recrystallisation (Found: C, 61·4; H, 3·5; N, 7·65; Cl, 15·0. Calc. for $C_{12}H_8O_2NCl$: C, 61·1; H, 3·4; N, 7·65; Cl, 15·2%). Turner and Le Fèvre[9] report the substance as forming almost colourless needles, m. p. 157—158°. Reduction of the nitro-compound with hydrazine hydrate in boiling absolute alcohol over a platinum–carbon catalyst gave 4-amino-4′-chlorodiphenyl (80%), crystallising from alcohol in plates, m. p. 132—133° (lit.,[10] 134°). The amine (2·0 g.) in glacial acetic acid (25 c.c.) was diazotised with sodium nitrite (0·7 g.) in concentrated sulphuric acid (6 c.c.) at 15—20°. The solution was poured on ice, then heated 1 hr. on a steam-bath; when cold, the 4-chloro-4′-hydroxydiphenyl was collected and crystallised from light petroleum (b. p. 60—80°) in pale brown needles (0·9 g.), m. p. 143—144° (lit.,[11] 146—147°). From this, 3 : 5-dibromo-4′-chloro-4-methoxydiphenyl was prepared by the method previously described.[1]

3 : 5-*Dibromo*-3′-*chloro*-4-*methoxydiphenyl*.—3-Chloro-4′-methoxydiphenyl was prepared by an Ullmann condensation of *p*-iodoanisole[12] (79·5 g.) with *m*-chloroiodobenzene[13] (78·0 g.) and copper bronze (60 g.) at 260°. The reaction was sudden and violent. Cooling and extraction with ether gave a brown oil which slowly deposited much crystalline material. This was shown to be 4 : 4′-dimethoxydiphenyl by recrystallisation from alcohol (m. p. 172°; lit.,[14] m. p. 173°). The filtrate on evaporation gave a brown oil (38 g.) which was fractionally distilled in a vacuum. The fraction (16·0 g.) of b. p. 141—145°/0·8 mm. crystallised. Three recrystallisations from alcohol yielded 3-*chloro*-4′-*methoxydiphenyl*, needles (3·1 g.), m. p. 52—53° (Found: C, 70·9; H, 4·1; Cl, 15·7; OMe, 13·7. $C_{13}H_{11}OCl$ requires C, 71·3; H, 5·0; Cl, 16·2; $OCH_3$, 14·1%). This product (1·8 g.) on demethylation with hydrobromic acid in acetic acid followed by recrystallisation from light petroleum (b. p. 60—80°)–chloroform gave 3-*chloro*-4′-*hydroxydiphenyl* (1·2 g.), plates, m. p. 98·5—99·5°. Treatment of this compound with bromine (2 g.) with a trace of iron powder in carbon disulphide (20 c.c.) at room temperature for 2 days gave 3 : 5-dibromo-3′-chloro-4-hydroxydiphenyl, which after repeated recrystallisation from light petroleum (b. p. 60—80°) formed needles, m. p. 122—123°. Methylation (diazomethane) and repeated recrystallisation from alcohol gave the *methyl ether* (0·2 g.) as plates,

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[9] Le Fèvre and Turner, *J.*, 1928, 253.
[10] Gelmo, *Ber.*, 1906, **39**, 4176.
[11] Angeletti and Gatti, *Gazzetta*, 1928, **58**, 633.
[12] Reverdin, *Ber.*, 1896, **29**, 4176.
[13] Klages and Liecker, *J. prakt. Chem.*, 1918, **61**, 321.
[14] Ullmann and Lowenthal, *Annalen*, 1904, **332**, 67.

m. p. 134·5—135·5° (Found: C, 40·6; H, 3·1; Br, 41·3; Cl, 9·7. $C_{13}H_9OBr_2Cl$ requires C, 41·5; H, 3·1; Br, 42·5; Cl, 9·4%).

3 : 5-*Dibromo*-2′-*chloro*-4-*methoxydiphenyl.*—This was prepared by the method described previously.[1]

Queen Mary College,
Mile End Road, London, E.1.

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