185. *The Thermal Decomposition of* 3 : 5-*Dibromobenzene*-1 : 4-*diazo-oxide.*

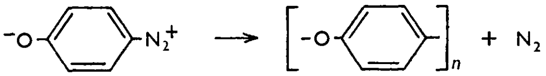
By M. J. S. Dewar and A. N. James.

3 : 5-Dibromobenzene-1 : 4-diazo-oxide decomposes in chlorobenzene above 70° to give nitrogen, bromine, and thermally stable polymers. These appear to be copolymers of bromochlorodiphenylyloxy- and dibromophenoxy-units. The mechanism of the reaction is discussed in terms of diradical intermediates and radical substitutions.

This paper describes part of a programme directed to the synthesis of polymers stable to heat. In view of the known thermal stability of diphenyl ether, it seemed to us that polyphenylene oxides might be of interest if they could be suitably synthesised.

In preliminary work we prepared polymers of this type from sodium *m*- and *p*-halogenophenoxides; the conditions required were, however, drastic, and the polymers were less stable than we expected. It seemed likely that the drastic conditions had led to side-reactions and introduction of labile groups into the polymers. We therefore sought a less violent synthesis.

One possibility seemed to be the thermal decomposition of benzene-1 : 4-diazo-oxides:



Reactions of this type have been observed in the photochemical decomposition of various solid diazo-oxides by Süss, Müller, and Heiss,[1] but the thermal decompositions have been little studied. Vaughan and Phillips [2] examined the thermal decomposition of various nitrobenzenediazo-oxides, but without sufficiently characterising the products.

To avoid side reactions it was necessary to block the reactive positions *ortho* to oxygen in the diazo-oxide; we therefore worked with the 3 : 5-dibromo- and the 3 : 5-dichloro-derivative which are easily prepared, relatively stable, and have both *ortho*-positions blocked. For safety we used solutions of the diazo-oxides, although Süss *et al.* found the photolysis of diazo-oxides dissolved in aromatic solvents to follow a different course to that in the solid state; they obtained *p*-arylphenols in which molecules of solvent had replaced the diazo-group. The need for caution was, however, shown by an accident in which 70 g. of diazo-oxide detonated on gentle rubbing.

3 : 5-Dibromobenzene-1 : 4-diazo-oxide (I) was prepared fairly pure by Böhmer's method,[3] and its solutions in chlorobenzene decomposed smoothly at $>70°$. The theoretical amount of nitrogen was evolved, together with much free bromine, and deep red solutions were formed from which we isolated polymers, a little *s*-tribromophenol, and tar. The polymers sintered at 200—220°, were soluble in benzene, chloroform, or bromoform, and insoluble in alcohol, acetone, or light petroleum, and their molecular weights lay in the range 1600—3600. They were unaffected by strong acids or alkalis and by reducing agents, but they were attacked by strong oxidising agents. Analysis showed them to contain both chlorine and bromine, indicating that solvent molecules had been incorporated; this was confirmed by oxidative degradation to *p*-chlorobenzoic acid.

Treating the polymers with alkali or reducing agents failed to give definite products; but an indication of their structure was provided when the diazo-oxide was decomposed in chlorobenzene containing 1% of methanol or water. Under these conditions the yield of polymer was greatly reduced, and considerable quantities of phenols of lower molecular weight were formed. In addition to *s*-tribromophenol, two new isomeric phenols

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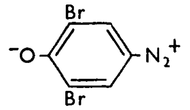
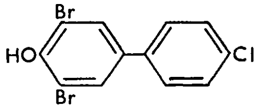
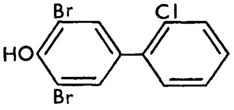
[1] Süss, Müller, and Heiss, *Annalen*, 1956, **598**, 123.
[2] Vaughan and Phillips, *J.*, 1947, 1560.
[3] Bohmer, *J. prakt. Chem.*, 1881, **24**, 453.

$C_{12}H_7OClBr_2$ were isolated. The work of Süss *et al.*[1] suggested very strongly that these were derivatives of 2 : 6-dibromophenol with a chlorophenyl group in the 4-position. We, therefore, synthesised 3 : 5-dibromo-4′-chloro-4-hydroxydiphenyl (II) by standard methods, and found it to be identical with one of the two phenols from our reaction; the isomeric phenol was presumably the 2′-chloro-isomer (III) since it gave *o*-chlorobenzoic acid on oxidation.


(I)


(II)

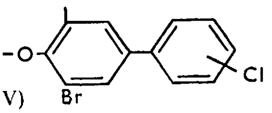

(III)

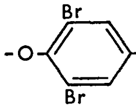
These results suggested that analogous diphenyl units might be present in the polymer. Table 1 shows the analyses of polymers prepared by heating (*B*) homogeneous solutions of the diazo-oxide and (*A*) a mixture of excess of solid diazo-oxide with the saturated solution; the calculated figures refer to a copolymer of (IV) and (V) in the proportions indicated in the last column. The agreement between calculated and observed figures is reasonable considering that end-groups have been neglected although the molecular weights of the polymers were not very high. The only real discrepancy appears in the hydrogen analyses which are uniformly too high (see below).

TABLE 1. *Composition (%) of polymers formed under various conditions.*

	Conditions		C	H	Br	Cl	O	(IV) (%)
A	27 hr./72°	Calc.	45·6	1·8	37·3	9·1	5·9	75
		Found	45·6	2·3	38·8	6·7	6·8	
A	4½ hr./85°	Calc.	46·6	1·9	35·6	9·7	5·8	79
		Found	46·6	2·3	38·5	7·1	6·7	
B	1 hr./110°	Calc.	48·4	2·0	32·8	10·8	5·8	88
		Found	48·4	2·6	31·6	10·4	6·3	
A	1 hr./110°	Calc.	42·3	1·6	42·6	7·7	6·0	60
		Found	42·3	2·0	43·9	4·5	6·4	
B	1 hr./131°	Calc.	49·6	2·0	31·0	11·4	5·7	93
		Found	49·6	2·5	30·8	9·9	6·6	
A	1 hr./131°	Calc.	43·8	1·7	40·0	8·2	5·9	67
		Found	43·8	2·2	37·1	8·6	6·8	
A	1 hr./131°; (+ 1% of MeOH)	Calc.	41·8	1·6	43·2	7·1	6·0	58
		Found	41·8	2·1	39·6	9·2	6·9	
B	Dichlorodiazo-oxide 1 hr./95°	Calc.	58·6	2·5	—	30·1	6·9	*
		Found	58·6	3·4	—	31·2	6·7	

* Calc. for 94% of $C_{12}H_6OCl_2$.


(IV)


(V)

Similar results were obtained on thermal decomposition of 3 : 5-dichlorobenzene-1 : 4-diazo-oxide in chlorobenzene. Nitrogen and chlorine were evolved and polymers were obtained with analyses analogous to those from the dibromodiazo-oxide, together with a little *s*-trichlorophenol. An example is given in Table 1.

The rate of evolution of nitrogen from the oxide (I) was investigated at several temperatures. Plotting log $V_\infty/(V_\infty - V_t)$ against V_t gives two intersecting straight lines, one of which passes close to the origin (see Figure). The apparent presence of two first-order stages is not understood. The first-order rate constants and derived activation energies are shown in Table 2.

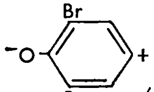
Mechanism.—The salient features of the reactions are the evolution of free halogen and the incorporation of molecules of solvent into the polymer. These suggest very

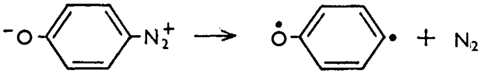
TABLE 2. *Rate constants and activation energies for the two stages in the decomposition of oxide* (I) *in chlorobenzene.*

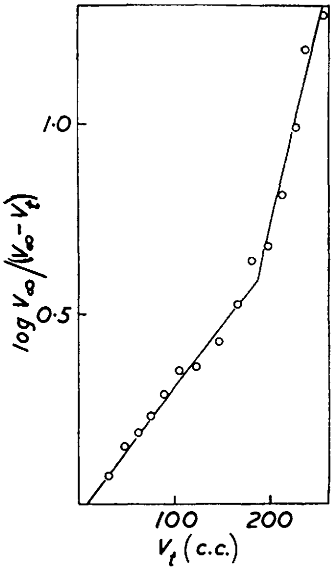
Temp.	72·3°	78·2°	81·3°	90·5°	101°	110°
10^4k_1 (sec.$^{-1}$)	1·55	3·43	5·61	12·1	31·7	70·8
10^4k_2 (sec.$^{-1}$)	4·08	8·75	8·31	12·1	19·7	22·8

E_1 = 25 kcal./mole. E_2 = 11 kcal./mole.

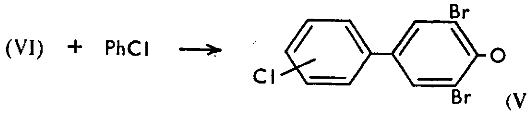
strongly that we are dealing with free-radical intermediates. Now loss of nitrogen from the diazo-oxide (I) might give a zwitterion (A) in which the + sign indicates that one sp^2-hybrid orbital of the ring carbon is empty. However, the binding energy of electrons attached to C^+ must be high, and the binding energy of the most weakly held π-electrons in the phenoxide ion low; it seems very likely, therefore, that particularly under non-polar conditions, the diradical structure (VI) would be more stable than the zwitterion. This diradical is derived from the zwitterion by transference of one π-electron into the unshared sp^2-orbital of the *para*-carbon atom. Note that the zwitterion and the diradical (VI) are distinct and not components of a hybrid; they differ in symmetry, since the sp^2 carbon orbital is symmetric, and the π-orbitals are antisymmetric, with respect to the plane of the ring. For the same reason there will be little coupling between the two unpaired electrons in the diradical, so it will behave as a genuine diradical.


(A)


(I) (VI)

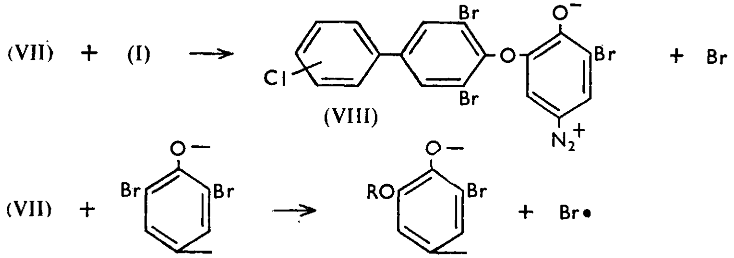


Rate of decomposition of 3 : 5-*dibromobenzene*-1 : 4-*diazo-oxide in chlorobenzene at* 72°.


(VII)

Now the σ-radical centre in (VI) (*i.e.*, the odd electron in the sp^2 carbon atomic orbital) will not differ appreciably from that in a free phenyl radical; this centre should be extremely reactive, and in particular should be able to attack the solvent by radical substitution, giving a diphenylyloxy-radical (VII); formally a hydrogen atom would be evolved in this process, but in practice it would be expected to remain attached to the chlorophenyl ring; disproportionation would eventually give rise to products containing *cyclo*hexadiene systems—which would explain the high hydrogen contents recorded in Table 1.

The other radical centre (π-radical centre) should be much less reactive, being analogous to that in the phenoxy-radical. Substitution into the solvent should therefore not occur here. However, radical displacement of bromine either from the diazo-oxide (I), or from a polymer molecule, should take place more readily, since the bromine should be somewhat activated by the adjacent oxygen atom and since C–Br bonds are relatively weak. In the former case a new diazo-oxide (VIII) will be formed, while the latter reaction is a propagation step in the growth of the polymer. In each case a bromine atom will be displaced, giving rise to the free bromine observed as a product of the reaction.



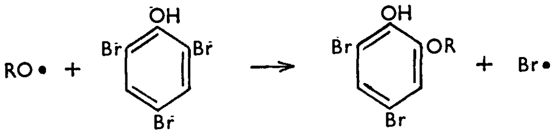
(VIII)

The inclusion of dibromophenoxy-units (V) in the polymer may be ascribed to coupling of the σ-radical centre of (VI), or the analogous diradical from (VIII), with the π-radical centres of monoradicals such as (VII) or of diradicals such as (VI). The formation of *s*-tribromophenol would arise from reaction of σ-radical centres with the free bromine formed in the reaction. Chains could be broken by reaction with the labile hydrogen atoms produced in the initial attack on the solvent.

Additional chain-breaking reactions could arise in the presence of water or methanol; reaction of water or methanol with free halogen would give rise to hydrogen bromide, which could act as a chain terminator: $RO\cdot + HBr \longrightarrow ROH + Br\cdot$. This would account for the formation of phenols of low molecular weight under these conditions. Bromine itself would not, of course, react effectively with radicals such as (VII); it could do so only by attacking carbon atoms in the phenoxide ring and so destroying its aromatic character.

This general mechanism is supported by the work of Hunter and his collaborators [4] who found that *s*-trihalogenophenols and related compounds were converted into polydihalogenophenylene oxides by oxidation. The mechanism which they suggested involved diradical intermediates; we consider it more likely that the mechanism is as follows, Ox representing the oxidising agent:

$$ROH + Ox \longrightarrow RO\bullet + (OxH)$$



In confirmation we have found that free halogen is evolved in reactions of this type. We have also found that oxidation of 3 : 5-dibromo-4′-chloro-4-hydroxydiphenyl (II) gives polymers, the intermediate, according to our formulation, being the same radical (VII) that we postulate as an intermediate in the diazo-oxide decomposition.

EXPERIMENTAL

3 : 5-*Dibromobenzene*-1 : 4-*diazo-oxide*.—The diazo-oxide was prepared according to Böhmer's directions [3] and dried before use. Recrystallisation from methanol did not alter the analysis or mode of decomposition significantly.

[4] Hunter *et al.*, *J. Amer. Chem. Soc.*, 1916, **38**, 1761; 1917, **39**, 2640; 1921, **43**, 131. 151; 1932, **54**, 1167.

3 : 5-*Dichlorobenzene*-1 : 4-*diazo-oxide*.—This *diazo-oxide* was prepared from the corresponding aminodichlorophenol by diazotisation, forming orange-brown needles (from methanol) exploding at 158° (Found: C, 38·9; H, 1·7; Cl, 37·5; N, 14·8. $C_6H_2ON_2Cl_2$ requires C, 38·1; H, 1·1; Cl, 37·5; N, 14·8%). Both compounds were dried over P_2O_5 *in vacuo* or by prolonged warming in an oven at 40°.

Decompositions of Diazo-oxides.—These were carried out on portions (2·78 g.) of compound (I) in varying quantities of chlorobenzene (fractionated from P_2O_5) in order to provide both heterogeneous and homogeneous conditions. Stirring was vigorous and temperature controlled. Bromine and solvent were removed at the water-pump, and the concentrated solutions were then filtered and poured into stirred methanol. The precipitated polymers were washed and dried at 100°, yielding 1·2—1·8 g. Evaporation of the methanol and extraction with alkali gave ~0·15 g. of *s*-tribromophenol, m. p. and mixed m. p. 96°

Bromine was estimated by sodium peroxide fusion of the polymer in a micro-Parr bomb, followed by oxidation of bromide to bromate with sodium hypochlorite and determination of bromate iodometrically. This method is a micro-modification of Haslam's macro-procedure.[5] Chlorine was calculated by difference from the total halide, thus giving an inherent error of ±10%. The results are shown in Table 1.

Isolation and Identification of Phenolic By-products.—The dibromodiazo-oxide (I) (139 g.) was decomposed in refluxing chlorobenzene (1 l.) containing methanol (10 c.c.). The polymer was removed in the usual way and the filtrate, after evaporation of the methanol, was extracted with alkali. The alkaline extracts were acidified and extracted with ether, and the ether extracts dried (Na_2SO_4) and evaporated. The phenolic residue was distilled, giving *s*-tribromophenol (12·2 g.), b. p. 120—124°/0·5 mm. The involatile residue was dissolved in hot alcohol, water was added, and later a large quantity of pink crystals was filtered off and recrystallised from benzene, to give three crops. The first crop, after repeated recrystallisation from alcohol and finally from light petroleum (b. p. 60—80°), gave almost white needles of 3 : 5-*dibromo*-4′-*chloro*-4-*hydroxydiphenyl*, m. p. 167·5—168·5° (Found: C, 39·9; H, 2·1; Br, 44·9; Cl, 10·9. $C_{12}H_7OClBr_2$ requires C, 39·8; H, 2·0; Br, 44·1; Cl, 9·8%); the *monomethyl ether*, prepared by diazomethane in ether, crystallised from alcohol in pale brown needles, m. p. 116·5—117·5° (Found: C, 40·2; H, 2·6; Br, 41·8; Cl, 10·2; OMe, 7·9. $C_{13}H_9OClBr_2$ requires C, 41·5; H, 2·4; Br, 42·5; Cl, 9·4; OMe, 8·2%). The second crop after several recrystallisations from aqueous alcohol and finally from light petroleum (b. p. 40—60°) gave slightly brown needles of 3 : 5-*dibromo*-2′-*chloro*-4-*hydroxydiphenyl*, m. p. 124—126° (Found: C, 39·6; H, 2·5; Br, 41·1; Cl, 9·8%), whose *monomethyl ether* crystallised from light petroleum (b. p. 40—60°) in white needles, m. p. 109—110° (Found: C, 41·2; H, 2·4; Br, 42·5; Cl, 9·4; OMe, 8·3%).

3 : 5-Dibromo-2′-chloro-4-hydroxydiphenyl with alkaline permanganate gave *o*-chlorobenzoic acid (10%), m. p. and mixed m. p. 138—139°.

The third crop of phenolic material did not yield any further product.

3 : 5-*Dibromo*-4′-*chloro*-4-*hydroxydiphenyl*.—4-Chloro-4′-methoxydiphenyl was prepared by the procedure used by Harley-Mason and Mann [6] for the corresponding bromo-compound. The crude ether fraction was distilled, under reduced pressure, through a column packed with glass helices. Two fractions were collected: (*a*) b. p. >140°/0·4 mm.; (*b*) b. p. 140—150°/0·4 mm. Fraction (*b*) deposited crystals which after recrystallisation from alcohol formed white needles, m. p. 110—111°, which on demethylation with hydrobromic acid in acetic acid and recrystallisation from light petroleum (b. p. 60—80°) gave 4′-chloro-4-hydroxydiphenyl, m. p. 145—146° (lit.,[7] 146—147°). Bromination of the phenol (1 g.) with bromine (1·76 g.) in carbon disulphide (10 c.c.) gave 3 : 5-dibromo-4′-chloro-4-hydroxydiphenyl, pale brown needles (0·8 g.) [from light petroleum (b. p. 60—80°)], m. p. 167·5—168·5° undepressed on admixture with the specimen prepared as above.

4′-*Chloro*-2-*methoxydiphenyl*.—Fraction (*a*) above, on crystallisation from methanol, gave prismatic needles, m. p. 50—52°, which by analogy with the work of Harley-Mason and Mann were assumed to be 4′-*chloro*-2-*methoxydiphenyl* (Found: C, 71·1; H, 5·1; OMe, 14·4. $C_{13}H_{11}OCl$ requires C, 71·4; H, 5·1; OMe, 14·2%).

Attempts to prepare 2′-chloro-4-methoxydiphenyl as a precursor of the phenol (III) from

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[5] Haslam, *Analyst*, 1950, **75**, 371.

[6] Harley-Mason and Mann, *J.*, 1940, 1379.

[7] Angeletti and Gotti, *Gazzetta*, 1929, **58**, 630.

anisole and *o*-chloroaniline, gave only 2′-chloro-2-methoxydiphenyl, m. p. 53—54° (lit.,[8] 53—54°).

Oxidation of Phenol (III).—Heating the phenol (0·23 g.) with lead dioxide (0·5 g.) in dry benzene (30 c.c.) in presence of sodium sulphate (0·1 g.) under reflux for 2 hr., followed by filtration, concentration, and pouring into methanol, gave a pink *polymer* (0·16 g., 90%), sintering at 300° [Found: C, 50·9; H, 2·3; Br, 28·0; Cl, 14·0. $(C_{12}H_6OClBr)_n$ requires C, 51·2; H, 2·2; Br, 28·4; Cl, 12·6%].

Measurements of Rates of Decomposition.—Measurements were carried out in a flat-bottomed glass tube, 4 cm. in diameter, 17 cm. long, fitted with a glass-sheathed magnetic paddle. The tube was held in a thermostat-bath and connected to a conventional gas burette. Dry chlorobenzene (50 c.c.) was placed in the tube and brought to the required temperature. The stirrer was started, a weighed amount (0·3475 g.) of diazo-oxide (I) added rapidly, and the apparatus closed. First-order rate constants were calculated in the usual way from plots of the volumes of gas evolved.

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[8] Mascarelli and Pirora, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1937, **26**, 243.