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NAPHTHAQUINONES—II

DERIVATIVES OF NAPHTHALENE-2,7-DIOL

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Abstract—The oxidation of 1,6-dibromo-2,7-dimethoxynaphthalene has been reinvestigated and the 1-bromodimethoxy-compound has yielded a new bromonaphthaquinone. A transbromination of 1,6-dibromonaphthalene-2,7-diol has been noticed, whilst an azo-dye from this dibromodiol is shown to have a structure different from that expected from the earlier literature.

As a sequel to recent work[1] the present paper concerns investigations relating mainly to the structures of the chief products of mono- and di-bromination of naphthalene-2,7-diol.

Cooke *et al.*[2] have prepared, for the first time, pure 1,6-dibromonaphthalene-2,7-diol and have indicated that the 1,8-dibromo-compound can be converted into the apparently more stable 1,6-dibromodiol by heating in hydrobromic acid in acetic acid. Full details of their methods do not appear to have been published,* but the present author has prepared pure 1,6-dibromonaphthalene-2,7-diol by chromatography on alumina. It seemed likely† that the crude product of attempted dibromination of naphthalene-2,7-diol consisted of mainly the 1,6- and 1,8-dibromo-derivatives. Thus treatment of this product with hydrobromic acid in acetic acid was expected to give a better yield of the 1,6-dibromo-compound by isomerization of the 1,8-dibromo-derivative in the mixture.[2] With hydrogen bromide in aqueous acetic acid an intermolecular change seemed to occur, since the only isolated compound was the 1,3,6-tribromodiol. To ensure that this result did not arise merely from the presence of the tribromo-compound in the starting material, a similar experiment was conducted on pure 1,6-dibromodiol. The only pure product obtained in this case, as also when water was omitted, was the tribromodiol. It appears, then, that, in the preparation of 1,6-dibromonaphthalene-2,7-diol by direct bromination, it is inadvisable to heat the reaction-mixture, since production of the tribromo-derivative may ensue in the medium containing hydrogen bromide as a product of the initial bromination.

The mechanism of this transbromination is presumably as indicated below.[4] Steric hindrance to substitution in the 8-position of the 1,6-dibromodiol would make the

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* The work of R. G. Cooke, B. L. Johnson and W. R. Owen has now been published in detail [*Austral. J. Chem.* **13**, 256 (1960)]. They have given evidence that the compound, which was earlier[3] thought to be the 1,8-dibromo-diol, is the 1,3-isomer.

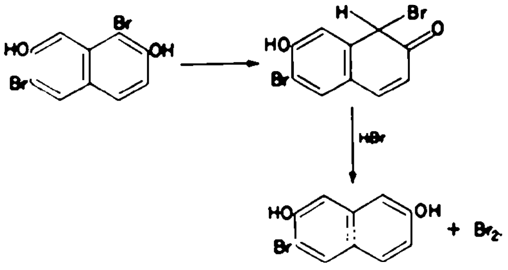
† See Ref. 2 and analytical results of Ref. 3.

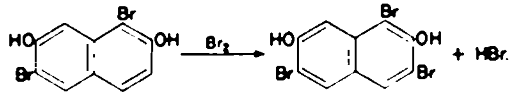
[1] R. D. Wilson, *Tetrahedron* **3**, 236 (1958).

[2] R. G. Cooke, B. L. Johnson and W. R. Owen, *Chem. & Ind.* 1623 (1957).

[3] I. S. Ioffe and N. M. Fedorova, *Zh. Obshchei Khim.* **6**, 1079 (1936); *Chem. Abstr.* **31**, 1022 (1937).

[4] R. H. Thomson, *Quart. Rev.* **10**, 32 (1956); P. B. D. de la Mare and J. H. Ridd, *Aromatic Substitution: Nitration and Halogenation* p. 123. Butterworths, London (1959); P. W. Robertson, *J. Chem. Soc.* 1883 (1956); H. Franzen and G. Stäuble, *J. Prakt. Chem.* **103**, 352 (1922); E. S. Lewis and M. C. R. Symons, *Quart. Rev.* **12**, 242 (1958).





1,3,6-tribromo-compound the main product of further bromination.[5] Regarding the structure of the tribromo-derivative, Cooke *et al.*[2] have made 3,6-dibromonaphthalene-2,7-diol by the reduction of the product of brominating naphthalene-2,7-diol with three moles of bromine per mole of the diol.* In view of the reduction of the 1,8-dibromodiol to the 3-bromodiol,[2] it is possible that reducing 1,3,8-tribromonaphthalene-2,7-diol would give the 3,6-dibromo-compound.

Ethylation of the 1,6-dibromodiol afforded crude material melting at about 85°. In preliminary work some difficulty was encountered in trying to obtain a pure compound, analyses indicating incomplete ethylation.

Methylation of the dichloronaphthalene-2,7-diol has been shown to give a product identical with that from the chlorination of 2,7-dimethoxynaphthalene.[1] Thus it is confirmed that naphthalene-2,7-diol and its dimethyl ether yield similarly orientated main products on direct dichlorination (cf. dibromination[6]).

Naphthaquinones

2,6- and 2,7-Dimethoxynaphthalenes were separately treated with chromic acid. By chromatography 2,7-dimethoxy-1,4-naphthaquinone has been prepared in a purer state than heretofore.[1,7] No pure compound was isolated from this oxidation of 2,6-dimethoxynaphthalene, but the use of a different oxidant† yielded the expected quinone as one of the products.

Oxidation of the product of direct monobromination of 2,7-dimethoxynaphthalene has, despite the use of chromatography, afforded only a bromo-2,7-dimethoxy-1,4-naphthaquinone, which is concluded to have the structure (I). Assigning this formula (5-bromo-3,6-dimethoxy-1,4-naphthaquinone) is compatible with the results of, first, the oxidation of 1,6-dibromo-2,7-dimethoxynaphthalene and, secondly, the bromination of 2,7-dimethoxy-1,4-naphthaquinone,[1,8] in which 6-bromo- (II) and 3-bromo-2,7-dimethoxy-1,4-naphthaquinone (III) were prepared. It is to be noted that these

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* See Ref. 1 on the result of the oxidation of 1,3,6-tribromo-2,7-dimethoxynaphthalene.

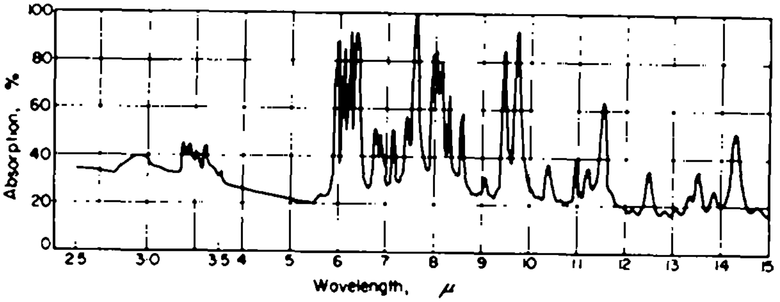
† Forthcoming paper.

[5] P. B. D. de la Mare and J. H. Ridd, *Aromatic Substitution: Nitration and Halogenation* p. 180. Butterworths, London (1959).

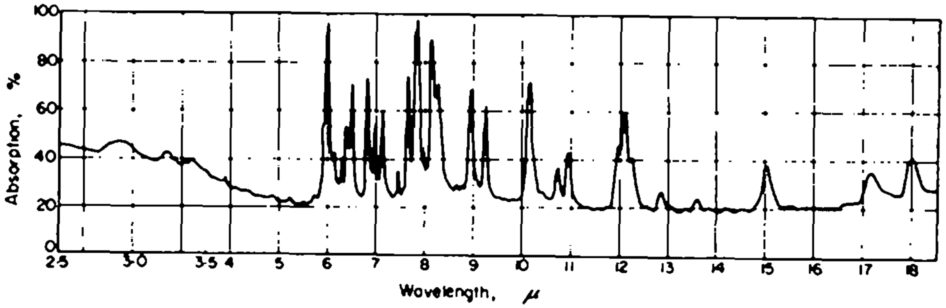
[6] F. Bell, J. A. Gibson and R. D. Wilson, *J. Chem. Soc.* 2335 (1956).

[7] L. F. Fieser and R. H. Brown, *J. Amer. Chem. Soc.* 71, 3615 (1949).

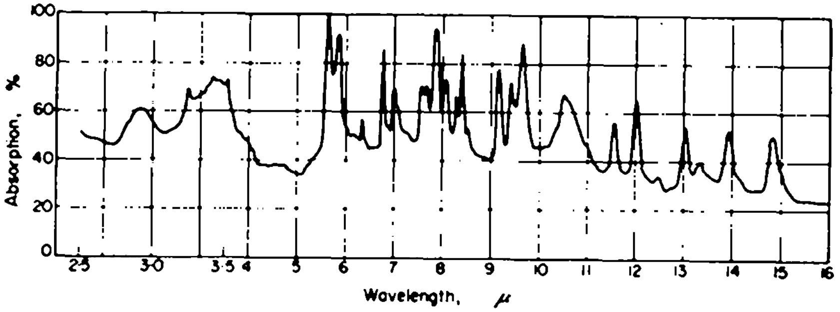
[8] P. B. D. de la Mare and J. H. Ridd, *Aromatic Substitution: Nitration and Halogenation* p. 185. Butterworths, London (1959).



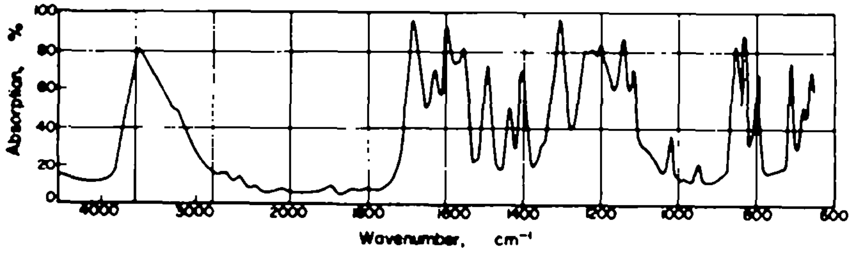
SPECTROGRAM 1.



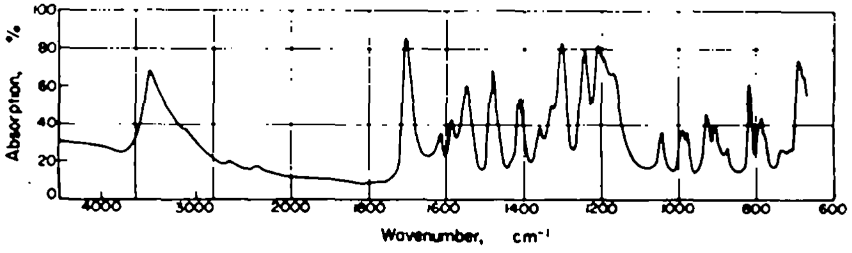
SPECTROGRAM 2.



SPECTROGRAM 3.



SPECTROGRAM 4.

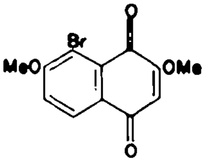


SPECTROGRAM 5.

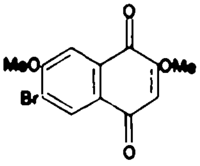
Number of spectrogram*	Name of compound	Percentage of compound in KBr	Thickness of disk (mm)
1	6-Bromo-2,7-dimethoxy-1,4-naphthaquinone	1	0·3
2	3,8-Dibromo-7-methoxy-1,2-naphthaquinone	1	0·3
3	5-Bromo-2-carboxy-4-methoxyphenylglyoxal	1	0·3
4	1,1,6-Trichloro-1,2-dihydro-7-hydroxy-2-oxonaphthalene	0·5	0·8
5	3,8-Dibromo-1,1,6-trichloro-1,2-dihydro-7-hydroxy-2-oxonaphthalene	0·5	1·0

* The spectra were obtained with a Grubb–Parsons double-beam spectrometer, using a KBr disk.

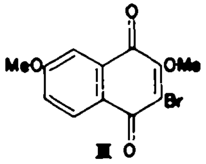
two compounds would be the only likely significant quinones from the oxidation of the product of monobromination of the dimethoxynaphthalene, if the claim of Ioffe and Fedorova, that monobromination of the 2,7-diol gave the 3-bromo-derivative, were correct.[3]



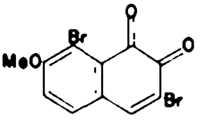
I



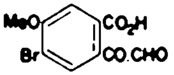
II



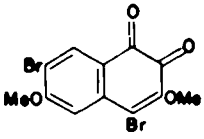
III



IV



V



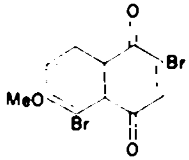
VI

The oxidation of 1,6-dibromo-2,7-dimethoxynaphthalene[1] has been repeated, and it has been possible to isolate purer specimens of the quinones (II, IV) and also an acid (V). The structure (VI) was previously[1] attributed to the 1,2-quinone (cf. the conversion of 1-tetralone into 1,2-naphthaquinone[9]). The determination of the contents of bromine, oxygen and methoxyl group now shows this to be incorrect. It is

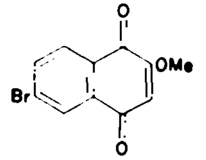
[9] T. Shoji, *J. Pharm. Soc. Japan* **79**, 1034 (1959).

interesting that, while the monobromodimethoxynaphthalene yields, on oxidation, the quinone with the bromine atom retained in the α-position, the dibromo-ether gives the 1,4-quinone with the α-bromine atom removed by the formation of a carbonyl group (cf. the oxidation of the dichloro-ether[1]). The latter result may be related to the inductive deactivation, by the 6-bromo-substituent, to electrophilic attack by the oxidant.[10] From the oxidation of 1,6-dibromo-2-methoxynaphthalene,[6] however, both 1,4-quinones (VII, VIII) were obtained. It is possible that the 7-methoxy-substituent in 1,6-dibromo-2,7-dimethoxynaphthalene impedes sterically the lateral displacement of the 6-bromine atom that may be necessary for the attack in the 5-position by the oxidant. The formation of the 1,2-quinone (IV) by removing the 7-methoxy-group from the dibromodimethoxynaphthalene then appears to be the preferred mode of oxidation of the ring bearing this methoxy-substituent. In the oxidation of 1,3,6-tribromo-2,7-dimethoxynaphthalene[1], in which the steric situation is even more congested, the α-bromine atom is displaced.

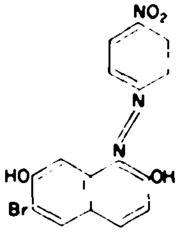
The microanalyses of the acidic product suggest an aldehydic and ketonic monocarboxylic acid. The spectrogram (3), showing strong bands at wavelengths of 5·6, 5·8 and 7·8 μ, is compatible with this.[11] The oxidation of the dibromo-ether seems likely, from the foregoing discussion, to involve preferential attack on the ring with the α-bromo-substituent. The bands at 11·5 and 12·0 μ suggest 1,2,4,5-tetrasubstitution as opposed to the possible 1,2,3,4-tetrasubstitution[12] in the acid, which would arise from rupture of the ring bearing the β-bromo-substituent. Under the influence of the methoxyl group the opening of the ring is then expected to occur between the 1- and 2-carbon atoms. A possible intermediate is an *o*-carboxycinnamic acid, which, on further oxidation, might give the compound V.



VII



VIII



IX

Coupling with diols

So far no success has attended efforts to identify, by reduction, the dyes prepared by coupling *p*-nitrobenzenediazonium chloride with 1-bromonaphthalene-2,7-diol and with the 1,6-dibromodiol. The products of coupling themselves appeared to be impure*, but in one case, from the reaction of 1,6-dibromonaphthalene-2,7-diol with the diazonium chloride, the analytical results suggest that the compound IX was formed. The coupling involving the displacement of the bromo-substituent (as in the

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* Cf. Ref. 3.

[10] W. A. Waters, *Quart. Rev.* **12**, 290 (1958); I. Necsoiu and C. D. Nenitzescu, *Chem. & Ind.* 377 (1960).

[11] E. Bernatek, *Tetrahedron* **4**, 216 (1958).

[12] L. J. Bellamy, *The Infrared Spectra of Complex Molecules* (2nd Ed.). Methuen, London (1958); A. D. Cross, *Introduction to Practical Infrared Spectroscopy*. Butterworths, London (1960).

coupling of 1-bromo-2-naphthol[13,14]) thus appears to occur to a significant extent despite the presence of the unsubstituted 8-position in the dibromodiol.

Ioffe and Fedorova[3] considered that the dibromodiol gave a bisazo-dye containing two atoms of bromine in the molecule. This result might be accounted for by the displacement of the α-bromo-substituent as hypobromous acid,[15] which, in the absence of thiosulphate, rebrominated the dye in the available 3-position. The product of such a reaction in an alkaline medium[16] would be, after acidification, 3,6-dibromo-1,8-bis-*p*-nitrobenzeneazonaphthalene-2,7-diol. In relation to this work the effect of thiosulphate on the yield of the bromine-free dye from the coupling of diazotized *p*-nitroaniline with 1-bromo-2-naphthol[15] is emphasized.

EXPERIMENTAL[*]

Purification of 1,6-*dibromonaphthalene*-2,7-*diol*

Crude dibromodiol (199 g; m.p. 152·5–153) was prepared as previously[17] from naphthalene-2,7-diol (101 g). Recrystallization from benzene, *o*-dichlorobenzene, or aqueous acetic acid (5 vols acetic acid : 2 vols water) seemed unpromising (cf. Ref. 3).

Some (5·38 g) of the product (m.p. 152·5–154·5°) of recrystallizing twice from benzene gave, with a mixture of benzene (106 ml) and chloroform (74 ml), a solution which was chromatographed on a column of alumina (46 cm high × 3·2 cm in diameter; column produced from a dispersion of alumina in benzene). Development with benzene produced a narrow, light brownish-grey band above a light cream-coloured band involving the remainder of the column. The latter band was divided into 3 equal portions, each of which was extracted with hot acetic acid. The solvent was removed from the extracts, and the residues were treated separately with hot acetic acid and decolourizing charcoal. Hot filtration was followed by dilution with water, to give precipitates which were filtered off. Recrystallization of the product (c) from a solution of acetic acid (2 vol) in water (1 vol) and then from glacial acetic acid afforded minute white needles (0·55 g) of 1,6-dibromonaphthalene-2,7-diol, m.p. 163–163·5° with sublimation. (Found: C, 38·0; H, 1·9; Br, 50·6. Calc. for $C_{10}H_6Br_2O_2$: C, 37·8; H, 1·9; Br, 50·3%). Crystallization (from benzene; cf. ref. 3) of a specimen melting at 162–162·5° gave a product with m.p. 162·5–163°.

Precipitate	W	m.p.
(a) From top third of band	0·85 g	142–148°
(b) From middle third of band	0·89 g	145–148·5°
(c) From lowest third of band	2·04 g	155·5–158°

Transbromination

(1) 1,6-Dibromonaphthalene-2,7-diol (0·55 g; m.p. 163–163·5), acetic acid (2·8 ml) and hydrobromic acid (1·4 ml; 48–50% w/w HBr; less than 0·01% w/v Br_2) were heated by a water-bath for 4 hr. The cold product was filtered (filtrate A), and the residue was washed with acetic acid (filtrate B), leaving a solid (0·20 g; m.p. 185·5–195·5°), which was extracted with boiling water. The aqueous

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[†] M.ps are corrected. Most of the microanalyses were carried out through Dr. A. Bernhardt, Mülheim, Germany.

[13] V. Veselý and F. Štursa, *Chem. Listy* **27**, 126 (1933); *Chem. Abstr.* **27**, 5320 (1933).

[14] J. T. Hewitt and H. V. Mitchell, *J. Chem. Soc.* **89**, 1167 (1906).

[15] I. S. Ioffe, *Zh. Obshchei Khim.* **6**, 1074 (1936); *Chem. Abstr.* **31**, 1021 (1937).

[16] P. B. D. de la Mare and J. H. Ridd, *Aromatic Substitution: Nitration and Halogenation* p. 114. Butterworths, London (1959); E. Šilov and N. Kaniaev, *Dokl. Akad. Nauk SSSR* **24**, 890 (1939).

[17] R. D. Wilson, Thesis for the Fellowship of the Heriot-Watt College, Edinburgh (1957).

extract was cooled and filtered, to give about 1 mg of residue, m.p. about 149°, and a filtrate which yielded only a trace of solid on removal of the solvent.

The solid left after extraction by boiling water melted at 190·5–196·5°. Repeated crystallization from acetic acid afforded minute white needles of 1,3,6-tribromonaphthalene-2,7-diol, m.p. 207–208·5° with sublimation. (Found: C, 30·3, 30·5; H, 1·6, 1·3; Br, 60·1. Calc. for $C_{10}H_5Br_3O_2$: C, 30·3; H, 1·3; Br, 60·4%).

The combined filtrates (A) and (B) were diluted to 25 ml with water. Filtration yielded a residue (C) and a solution, which, by removal of the solvent, gave 0·09 g of material, most of which was dissolved by warm chloroform. Removal of chloroform from the solution afforded only an unpromising substance.

The residue (C; 0·19 g; m.p. 142–143°) in toluene was chromatographed on alumina. Toluene was used for development. Removal of solvent from the eluate gave no residue. The column showed four bands, which were extruded. The narrow brownish-grey top band was discarded, whilst the others were extracted separately with hot acetic acid, the latter being subsequently removed from the extracts at 70–100°. The products from the second and third bands (in relation to top of column) were treated individually with 95% ethanol and charcoal. Removal of the charcoal and then the solvent gave impure materials. The product from the fourth band (light grey-blue) was treated with hot 95% ethanol (charcoal). Filtration and addition of water to the filtrate afforded a light grey solid (0·04 g; m.p. 154·5–156°), probably impure dibromodiol.

(2) Impure dibromodiol (7·85 g; m.p. 151·5–153·5°), by heating for 1 hr under similar conditions, gave a residue (D; 2·30 g; m.p. 179–183°) and a filtrate, which was diluted to 500 ml with water, to afford a precipitate (E; 4·36 g; m.p. 145–146°). The m.p. of a mixture of D and E in the proportions in which they had been yielded (28 mg : 53 mg) was 142·5–145·5°. Repeated crystallization (charcoal) of D from acetic acid afforded material m.p. 201·5–203·5° (mixed m.p. with tribromo-compound, m.p. 196·5–198°, made by direct bromination of the 2,7-diol[17] was 199–200·5°). A further crystallization from acetic acid gave minute white needles, 0·47 g; m.p. 205·5–206·5°. (Found: C, 30·8; H, 1·5%). Repeated crystallization (charcoal) of E from acetic acid gave a product, 1·01 g; m.p. 155·5–157°.

(3) Impure dibromodiol (7·85 g; m.p. 151·5–153·5°), acetic acid (25 ml) and a solution of hydrogen bromide in acetic acid (30 ml; 50% w/v HBr; less than 0·1% w/v Br_2) were heated (reflux condenser with $CaBr_2$) in a bath at 100° for 1 hr. The cold product was filtered, to give only a trace of residue. The filtrate was diluted with water to 250 ml, and the resulting precipitate was filtered off and washed with water. The product (5·5 g; m.p. 136·5–140·5°) was crystallized twice from benzene (charcoal), giving a substance (1·1 g) m.p. 165–178°. Repeated crystallization from acetic acid (charcoal) yielded a solid (0·06 g; m.p. 206–208°). Mixed m.p. with tribromonaphthalenediol (m.p. 207–208·5°; as mentioned in section (1) under "Transbromination") was 207–208·5°.

1,6-*Dibromo-2,7-diethoxynaphthalene*

A mixture of impure 1,6-dibromonaphthalene-2,7-diol (8·2 g; m.p. 151·5–153·5°) dissolved in acetone ("AnalaR"; 80 ml), potassium carbonate ("AnalaR"; 6·5 g) and diethyl sulphate (9·3 ml) was refluxed for 30 min. The product was concentrated by removal of distillate (40 ml), diluted with water to 250 ml, and then maintained at 40° for 2 hr. Addition of 2 N NaOH (60 ml) preceded further heating at 40° for 1 hr. Filtration and washing of the residue with water afforded a solid (7·1 g), m.p. 77° to above 86°, which was treated with boiling 95% ethanol and charcoal before hot filtration (filtrate F). The residue was agitated with boiling acetic acid and filtered, to leave white crystals (0·26 g; m.p. 154–155·5°; insoluble in boiling 2 N NaOH). Recrystallization from acetic acid gave 1,6-*dibromo-2,7-diethoxynaphthalene* as white plates, m.p. 154·5–155·5° and mixed m.p. with pure dibromodiol 135–147° (Found: C, 45·3; H, 3·8; Br, 43·0; EtO, 24·0. $C_{14}H_{14}Br_2O_2$ requires: C, 44·9; H, 3·8; Br, 42·7; EtO, 24·1%).

The filtrate (F) yielded, on cooling, a solid, which, by crystallization from 95% ethanol and then *o*-xylene (charcoal), afforded a product (0·35 g) with a melting range around 145°.

The solvent was removed at reduced pressure from the mother-liquor from the last crystallization. The residue was recrystallized from 95% ethanol, to give a solid (2·5 g), m.p. 81–91°. Chromatography, on cellulose powder, of a solution in benzene/chloroform and, on alumina, of a solution in benzene did not achieve the isolation of a pure compound. Analyses (in particular, for ethoxyl group) suggested mixtures of mono- and di-ethyl ethers of the dibromodiol.

1,6-*Dichloro-2,7-dimethoxynaphthalene*

1,6-Dichloronaphthalene-2,7-diol (designated earlier[4] as "1,8-dichloro-2,7-dihydroxynaphthalene") was prepared by the reduction, with zinc and acetic acid, of 1,1,6-trichloro-1,2-dihydro-7-hydroxy-2-oxonaphthalene,[17] previously[4] thought to be the 1,1,8-trichloro-compound (spectrogram (4); the spectrogram (5) of a related dibromotrichloro-compound is also shown). Methylation of the dichlorodiol (0·17 g) with dimethyl sulphate in aqueous sodium hydroxide gave a product (0·10 g), m.p. 142°. By recrystallization from acetic acid (charcoal) were obtained prisms, m.p. 143° and mixed m.p. with the product[1] of dichlorination of 2,7-dimethoxynaphthalene 142·5–143·5°.

2,7-*Dimethoxy*-1,4-*naphthaquinone*

2,7-Dimethoxynaphthalene (9·34 g) was oxidized as previously.[1] The resulting mixture was diluted with water (400 ml) and extracted repeatedly with 1,2-dichloroethane, the last extract being colourless. The solvent was removed from the extract after drying (Na_2SO_4), to give a solid (3·92 g) A solution of this in chloroform (100 ml) was chromatographed on alumina. Development by chloroform yielded five small brown bands at the top of the column and, at the bottom, a broad yellow band, which was eluted. Removal of the solvent from the eluate gave an orange-yellow solid (1·75 g), m.p. 211–222°. The product of recrystallization from acetic acid was washed with aqueous sodium hydrogen carbonate and then with water. The resultant yellow prisms (1·46 g) melted at 215–216° with sublimation. A mixed m.p. of 214·5–216° was obtained with 2,7-dimethoxy-1,4-naphthaquinone, m.p. 214–215° (Found: C, 66·2; H, 5·0. Calc. for $C_{12}H_{10}O_4$: C, 66·0; H, 4·6%), formed from 2,7-dimethoxynaphthalene by another oxidant.*

1-*Bromo*-2,7-*dimethoxynaphthalene*

2,7-Dimethoxynaphthalene (20·2 g) was monobrominated by the method previously described,[8] to give a product (19·2 g), m.p. 71–76°, which, on recrystallization from 95% ethanol, afforded white prisms (16·9 g), m.p. 75·5–76·5°. Crystallization of a portion (0·58 g) of the latter material from methanol yielded prisms (0·23 g), m.p. 77·5–78°.[8,18] (Found: C, 54·3; H, 3·8; Br, 30·4. Calc. for $C_{12}H_{11}BrO_2$: C, 54·0; H, 4·2; Br, 29·9%). A further crystallization (from 95% ethanol) did not change the m.p.

A more efficient method of preparation involved the addition of bromine as a dilute solution in chloroform. To dimethoxynaphthalene (3·08 g) in chloroform (30 ml) was added bromine (0·87 ml) in chloroform (100 ml) in 2·2 hr. The mixture was left in a closed vessel for 3 days at room temp. Removal of most of the solvent, subsequent filtration, and washing of the residue with chloroform yielded a product (3·27 g), melting at 75–77°. Recrystallization from methanol gave the bromo-compound (2·83 g), m.p. 77·5–78°.

Oxidation of 1-*bromo*-2,7-*dimethoxynaphthalene*

(1) A solution of chromium trioxide ("AnalaR"; 5·1 g) in water (4 ml) was added, from a burette in 4 min, to 1-bromo-2,7-dimethoxynaphthalene (1·65 g) in acetic acid (40 ml) and water (12 ml). Water (3 ml) was used to wash the residual chromic acid from the burette into the reaction mixture. After 15 min the product was diluted with water to 500 ml. Filtration and washing of the residue with water gave a light brown solid (0·66 g), m.p. about 213°, which, on treatment with boiling acetic acid and hot filtration, afforded a residue of light orange-brown prisms of the quinone (0·09 g; m.p. 299–302°; see Section 2 below) and a filtrate (5 ml). The latter was cooled and filtered, giving a residue (0·02 g, m.p. about 281–297°) and a filtrate, which was diluted with water to 100 ml, to produce a precipitate (0·42 g, m.p. below 169°). Chromatography on alumina failed to isolate a pure compound from this precipitate.

(2) To 1-bromo-2,7-dimethoxynaphthalene (2·83 g) in acetic acid (89 ml) was added chromium trioxide ("AnalaR"; 8·9 g) in water (18 ml) from a burette in 50 min. The maximum temp of the mixture was 46° (external cooling). The residual oxidant was washed from the burette into the mixture with water (4 ml). The product was then kept at 50° for 30 min. Dilution with water (800 ml) preceded filtration and washing of the residue (R) with water.

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* Forthcoming paper.

[18] R. Adams, M. W. Miller, F. C. McGrew and A. W. Anderson, *J. Amer. Chem. Soc.* 64, 1795 (1942).

The filtrate was extracted with chloroform. The dried (Na_2SO_4) and concentrated extract was chromatographed on alumina. After development by chloroform, the same solvent was used to elute the yellow lowest band. Seven other, small bands were discarded. The material obtained by removal of solvent from the eluate was crystallized twice from acetic acid, to yield yellow-orange prisms (S; 4 mg), m.p. 299·5 302·5°.

A solution of the residue (R; 0·50 g) in chloroform was chromatographed on alumina. Development with chloroform afforded a broad yellow band at the bottom of the column, an intermediate narrow yellow band, and a narrow brown band at the top of the column. The yellow bands were eluted by chloroform, whilst the brown portion of the column was extruded and extracted with hot acetic acid.

The eluate from the broad yellow band was collected in two portions, the first eluted having about three times the volume of the second. Removal of solvent from the larger portion, followed by recrystallization from acetic acid, gave deep yellow prisms (0·02 g), m.p. 300·5-302°, a trace of which yielded a purple solution with concentrated sulphuric acid. The mixture of this product and S (see above) was crystallized from acetic acid, to give deep yellow prisms of 5-*bromo*-3,6-*dimethoxy*-1,4-*naphthaquinone*, m.p. 302·5 304° with sublimation. (Found: C, 48·3; H, 3·1; Br, 27·2. $C_{12}H_9BrO_4$ requires: C, 48·5; H, 3·1; Br, 26·9%).

Removal of the solvent from the smaller portion of the eluate from the broad yellow band afforded only a small quantity of solid, m.p. 282-283°, presumably impure 5-bromo-3,6-dimethoxy-1,4-naphthaquinone.

Evaporation of the chloroform from the eluate from the narrow yellow band gave a trace of solid m.p. 153-189°.

The extract from the brown band was shown to contain a small quantity of an aromatic carboxylic acid, melting at about 203°.

(3) In the above oxidations the molar ratio of chromium trioxide to bromodimethoxynaphthalene was 8. The use of smaller proportions of the oxidant (molar ratios of 3 and 2) was less satisfactory. Wheeler and Mattox[19] employed a molar ratio of 5 for the oxidation of a derivative of naphthalene.

(4) Unchanged 1-bromo-2,7-dimethoxynaphthalene was the only compound isolated after an attempt to oxidize it with di-t-butyl chromate.[20]

Oxidation of 1,6-*dibromo*-2,7-*dimethoxynaphthalene*

Dibromodimethoxynaphthalene (73·5 g) was oxidized as before.[1] After dilution of the reaction product with water, filtration afforded a residue (K, 30·3 g), which was treated with toluene (1·2 l.). Subsequent filtration left a residue (2·5 g), which did not melt below 360° and of which a small proportion dissolved in aqueous sodium hydrogen carbonate.

The toluene solution was chromatographed (alumina). Development with toluene was followed by elution of the pink, lowest band with the same solvent, giving a yellow eluate (L). The column then showed a yellow band (at the bottom), a deep pink band, and several small, mainly dark brown bands (at the top). The yellow (M) and deep pink bands were extruded and separately extracted with hot acetic acid. The extract from the deep pink band was concentrated to 100 ml and then diluted with water to 400 ml. From the resulting precipitate (1·0 g) and also from the yellow eluate (L) no pure compound was isolable.

The extract from the yellow band (M) was concentrated and, after the addition of charcoal, was filtered while hot. The precipitate (N) from the cold filtrate was recrystallized from acetic acid, to yield a product (1·30 g), m.p. 258·5-260°. Three more crystallizations from acetic acid gave deep yellow acicular crystals of 6-bromo-2,7-dimethoxy-1,4-naphthaquinone, m.p. 260-260·5° (cf. Ref. 1; sublimate in m.p. tube). (Found: C, 48·7; H, 2·8; Br, 26·9. Calc. for $C_{12}H_9BrO_4$: C, 48·5; H, 3·1; Br, 26·9%).*

The aqueous filtrate from the residue K (see above) was extracted with chloroform. The solvent was removed from the dry (Na_2SO_4) extract, giving a very viscous material, which was treated with a mixture of acetic acid and petroleum ether (b.p. 80 100°). The product was filtered, and the residue was washed with acetic acid and then with water. The resulting solid (1·1 g) was with acetic agitated

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* See spectrogram (I) and cf. Sadtler spectrogram 15446 for the chloro-analogue.[1]

[19] A. S. Wheeler and W. J. Mattox, *J. Amer. Chem. Soc.* 55, 686 (1933).

[20] R. V. Oppenauer and H. Oberrauch, *Anal. Asoc. quim. Argentina* 37, 246 (1949); *Chem. Abstr.* **44**, 3871 (1950).

acid, the hot mixture being filtered to give a residue (P). The cold filtrate yielded a precipitate (0·7 g) which was treated with hot chloroform (80 ml). After cooling, the mixture was filtered (filtrate Q). Most of the residue dissolved, with effervescence, in aqueous sodium hydrogen carbonate. The addition of charcoal was followed by filtration and then by acidification of the filtrate with hydrochloric acid. The consequent white precipitate, after washing with water, weighed 0·29 g and m.p. was 229–229·5° (decomp). Two crystallizations from acetic acid afforded white prisms of *5-bromo-2-carboxy-4-methoxyphenylglyoxal* (V), m.p. 230·5–231·5° with decomp and white sublimation. (Found: C, 41·8; H, 2·5; Br, 27·7; O, 27·8; MeO, 10·6; equiv. wt. 278. $C_{10}H_7BrO_5$ requires: C, 41·8; H, 2·5; Br, 27·8; O, 27·9; MeO, 10·8%; equiv. wt. 287).* The compound gave a silver mirror with ammoniacal silver nitrate solution.

The filtrate (Q) was mixed with petroleum ether (120 ml; b.p. 80–100°), to precipitate a solid (0·21 g), which recrystallized from acetic acid as brownish-maroon needles, m.p. 236·5° (decomp). The latter material and the residue P (see above; 0·07 g) were crystallized thrice from acetic acid, yielding a product, which, after washing with aqueous sodium hydrogen carbonate and then with water, weighed 0·08 g and had m.p. 244°. Two further crystallizations from acetic acid gave deep brown-red needles of *3,8-dibromo-7-methoxy-1,2-naphthaquinone*, m.p. 244–244·5°. (Found: C, 38·0; H, 1·6; Br, 46·3; O, 14·3; MeO, 8·8. $C_{11}H_6Br_2O_3$ requires: C, 38·2; H, 1·7; Br, 46·2; O, 13·9; MeO, 9·0%).† A less pure specimen of this compound was formerly[1] designated as "4,7-dibromo-3,6-dimethoxy-1,2-naphthaquinone".

The mother-liquor from the precipitate (N) yielded, on dilution with an equal volume of water, a deposit which was recrystallized from acetic acid. The product, when it had been washed with aqueous sodium hydrogen carbonate and with water, was crystallized from a mixture (1 : 1 by volume) of petroleum ether (b.p. 80–100°) and toluene (charcoal) and then from acetic acid (charcoal), affording a substance (0·12 g), m.p. 125–128°. A final crystallization from methanol (charcoal) gave needles of 1,6-dibromo-2,7-dimethoxynaphthalene, m.p. 127·5–128·5° and mixed m.p. with an authentic sample 129–130°.

Coupling of p-*nitrobenzenediazonium chloride with bromo- and dibromo-naphthalene-2,7-diol*

Many experiments were done on the coupling of *p*-nitrobenzenediazonium chloride,[3] reduction of the resultant dyes and acetylation of the products of reduction. In only one case (see next paragraph) was an apparently pure compound isolated. Chromatography indicated complex mixtures. The dibromodiol used in the unsuccessful experiments melted at 151·5–154·5° (cf. Ref. 3).

To *p*-nitroaniline (0·23 g; 0·0017 mole) in 10 N HCl (0·50 ml) and water (0·60 ml) were added ice (2·5 g) and then sodium nitrite (0·132 g) in water (0·88 ml).[21] The solution of diazonium salt was poured into a solution of 1,6-dibromonaphthalene-2,7-diol (0·26 g; 0·00082 mole; m.p. 162·5–163°), sodium thiosulphate[15] (pentahydrate; 0·22 g), and sodium hydroxide (0·35 g) in water (4 ml). The product was acidified with N HCl (10 ml). The amorphous reddish-brown washed (water) dye (0·4 g), m.p. 195° (decomp), was recrystallized from a filtered solution in cold pyridine, to give the deep reddish-brown amorphous *6-bromo-1-*p-*nitrobenzeneazonaphthalene-2,7-diol* (0·07 g), m.p. 270° (decomp). (Found: C, 50·1; H, 2·9; Br, 21·0; N, 11·3. $C_{16}H_{10}BrN_3O_4$ requires: C, 49·5; H, 2·6; Br, 20·6; N, 10·8%). The compound formed, in concentrated sulphuric acid, a deep purple solution, which, on dilution with water, gave a red-brown solution.

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* See spectrogram (3).

† See spectrogram (2).

[21] K. H. Saunders, *The Aromatic Diazo-compounds and Their Technical Applications* (2nd Ed.) p. 6. **Arnold**, London (1949).