Tetrahedron, 1958, Vol. 3, pp 236-242. Pergamon Press Ltd., London

NAPHTHAQUINONES—I

THE MOLECULAR STRUCTURES OF SOME HALOGENO-2:7-DIHYDROXYNAPHTHALENES

R. D. WILSON
Stockport College, Wellington Road South, Stockport

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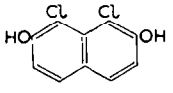
Abstract—Some new substituted naphthaquinones have been prepared by the oxidation of derivatives of 2:7-dimethoxynaphthalene with chromic acid. From an examination of the experimental results recorded in this paper and of some already available in the literature, it is now concluded that monobromination of 2:7-dihydroxynaphthalene gives the 1-bromo derivative and that dibromination and dichlorination furnish the 1:6-dibromo and 1:6-dichloro compounds.

IT has previously been shown[1,2] that the dibromination and dichlorination of 2:7-dihydroxynaphthalene give either 3:6-dibromo- and 1:8-dichloro-2:7-dihydroxynaphthalene (I, II) or the 1:6-dihalogeno derivatives (III, IV). Dibromination of the



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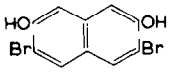

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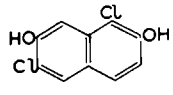

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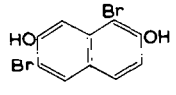
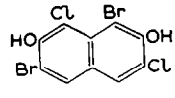


(IV)

dichloro-2:7-dihydroxynaphthalene was found to yield the same product as dichlorination of the dibromodiol. The absence of an atom of halogen in the 4-position (and in the 5-position, on the basis of the expected symmetry) is implied from the preparation of the yellow compound, 3:8-dibromo-6-chloro-2:7-dimethoxy-1:4-naphthaquinone (VI), by the oxidation, with chromic acid in acetic acid, of the dimethyl ether of



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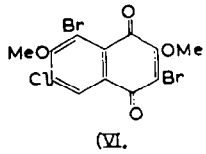


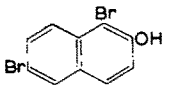
(VI.

the tetrahalogenodiol. The latter compound is now thought to be represented by the formula (V). It may be noted that, despite the lack of activation of the 4-carbon atom

[1] F. Bell, J. A. Gibson and R. D. Wilson, *J. Chem. Soc.* 2335 (1956).
[2] R. D. Wilson, Thesis for the Fellowship of the Heriot-Watt College, Edinburgh (1957).

by the hydroxyl group,[3] 1-chloro-2-naphthol yields, on chlorination, the 1:4-dichloro compound,[4,5] through the decomposition of an addition compound.

There will be discussed the significance of the experiments of some other workers in relation to the structure of the monobromo-2:7-dihydroxynaphthalene and hence to the molecular configurations of other halogeno derivatives of the diol. The preparations of various naphthaquinones described in this paper will then be shown to provide support for the contention[2] that the dichlorination and dibromination of 2:7-dihydroxynaphthalene both yield products (III, IV) that are analogous to the compound (VII) from the dibromination of 2-naphthol.[6,7]



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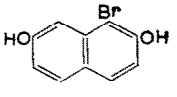
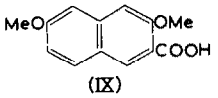


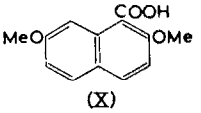
(VIII)

Discussion of molecular structures of some halogeno-2:7-dihydroxynaphthalenes and their methyl ethers

It is necessary as a preliminary to emphasise certain facts. First, the products of the mono-, di- and tri-bromination of 2:7-dimethoxynaphthalene are identical with the dimethyl ethers formed from the mono-, di- and tri-bromo-2:7-diols (VIII, IV and XVI), respectively (see Bell *et al.*[1] and under "Experimental"). It follows then that the mono-, di- and tri-bromination of 2:7-dihydroxynaphthalene give products that are structurally similar to those from the corresponding halogenations of the dimethyl ether, assuming that no quite unexpected rearrangement occurs during etherification. Secondly, the molecular structures of two 2:7-dimethoxynaphthoic acids are known. Sunthankar and Gilman[8] made the 3-naphthoic acid (IX) by acidification of the



(IX)

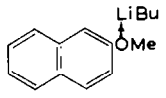


(X)

product of carbonation of the lithio derivative of 2:7-dimethoxynaphthalene. The structure of this acid, also obtained by Buu-Hoï and Lavit[9] by the oxidation of 3-acetyl-2:7-dimethoxynaphthalene, obtained from the Friedel–Crafts acetylation of the dimethoxynaphthalene, was determined by demethylation to the dihydroxynaphthoic acid. The latter had been prepared by Schmid,[10] who considered it was the 3-naphthoic acid in view of the difficulty of decarboxylation. Sunthankar and Gilman gave further support for this structure by obtaining, from 2:7-dimethoxynaphthalene by their general method of using lithio compounds, a 2:7-dihydroxynaphthalenedicarboxylic acid, one molecule of which coupled with two molecules of diazotised sulphanilamide. The other 2:7-dimethoxynaphthoic acid, afforded by the oxidation of the corresponding

[3] M. J. S. Dewar, *The Electronic Theory of Organic Chemistry* p. 175. Oxford University Press, Oxford (1949).
[4] P. M. James and D. Woodcock, *J. Chem. Soc.* 1931 (1951).
[5] P. W. Robertson, *J. Chem. Soc.* 1883 (1956).
[6] A. J. Smith, *J. Chem. Soc.* **35**, 789 (1879).
[7] H. E. Armstrong and E. C. Rossiter, *Proc. Chem. Soc.* **5**, 71 (1889).
[8] S. V. Sunthankar and H. Gilman, *J. Org. Chem.* **16**, 8 (1951).
[9] Ng. Ph. Buu-Hoï and D. Lavit, *J. Chem. Soc.* 1743 (1956).
[10] J. Schmid, *Ber. Dtsch. Chem. Ges.* **26**, 1114 (1893).

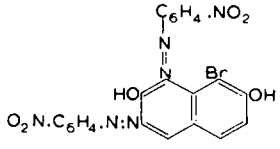
naphthaldehyde,[9,11] must therefore have the formula (X). The aldehyde, prepared by the methylation of the product of a Gattermann synthesis using the 2:7-diol[11] or by formylation of 2:7-dimethoxynaphthalene with dimethylformamide and phosphorus oxychloride,[12] would be expected to have the formyl group (of small effective bulk) on the 1-carbon atom. On the other hand, as pointed out by Sunthankar and Gilman, the formation of a lithio compound probably involves an intermediate co-ordination complex (XI), from the 3-position of which a proton is removed by nucleophilic attack by a carbanion from the reagent, *n*-butyl-lithium. There follows the attaching of a lithium cation to the 3-carbon atom.



(XI)

(XII)

(XIII)



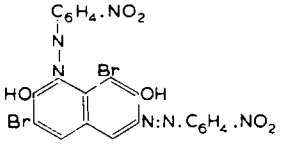
(XIV)

Now Adams *et al.*[11] obtained the 1-naphthoic acid (X) from the bromo 2:7-dimethoxynaphthalene by the action of *n*-butyl-lithium, followed by carbonation and treatment with hydrochloric acid. Thus it is proved that the product of the monobromination of 2:7-dihydroxynaphthalene must be the 1-bromo compound (VIII). Since the dibromo derivative has been shown to be either 1:6- or 3:6-dibromo-2:7-dihydroxynaphthalene,[1] it must now be concluded that it is actually the former (IV). From the earlier remarks 2:7-dimethoxynaphthalene must similarly yield the 1-bromo and 1:6-dibromo derivatives. In view of the recognised marked reactivity of the 1- and 8-positions in 2:7-dihydroxynaphthalene owing to electronic factors,[3] the entry of the second bromine atom into the 6-position is attributed to steric hindrance.

The only experimental work that does not at once appear to confirm these conclusions is due to Ioffe and Fedorova.[13] They found that one molecule of the bromo-2:7-diol or of the dibromo compound coupled with two molecules of diazotised *p*-nitroaniline, and they believed the products were the compounds (XII) and (XIII), respectively. Their results are, however, open to various other interpretations. For example, it is possible that coupling, involving an electrophilic attack,[14] takes place in the 6- and 8-positions in the monobromodiol and at the 3- and 8-carbon atoms in the dibromo compound, to give the products (XIV) and (XV), despite the known inertness of the 3-position in 1-methyl-2-naphthol[3] and the displacement of a bromine atom from the 1-carbon atom on treating 1-bromo-2-naphthol with diazotised *p*-nitroaniline. It is worthy of note that the primary isolable product in this last

[11] R. Adams, M. W. Miller, F. C. McGrew and A. W. Anderson, *J. Amer. Chem. Soc.* **64**, 1795 (1942).
[12] Ng. Ph. Buu-Hoï and D. Lavit, *J. Chem. Soc.* 2776 (1955).
[13] I. S. Ioffe and N. M. Fedorova, *J. Gen. Chem., U.S.S.R.* **6**, 1079 (1936); *Chem. Abstr.* **31**, 1022 (1937).
[14] C. K. Ingold, *Structure and Mechanism in Organic Chemistry* p. 297. Bell, London (1953).

reaction is probably the *p*-nitrobenzenediazo ether of 1-bromo-2-naphthol (XXII).[15,16] The coupling reactions are being further investigated experimentally. Ioffe and Fedorova made also the tribromodiol, the structure of which was indicated by the formula (XVI). This agrees with the present conclusions, when steric hindrance to substitution in the 8-position is considered.



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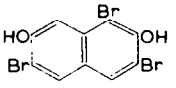


(XVI)

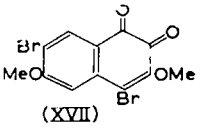
From the opening remarks in the introduction to this paper it is seen that the dichloro- and the dibromodichloro-2:7-dihydroxynaphtahlenes have the formulae (III) and (V), respectively. The dimethyl ethers corresponding to these halogenated diols (XVI, III and V) must have analogous structures.

Adams and his colleagues[11] were seeking optical activity due to the restricted rotation of groups in the *peri*-positions of derivatives of naphthalene. Their lack of success may be explained on the basis of the foregoing discussion. For example, it now seems that the compound, to which they ascribed the formula (XXIII), is correctly represented by the structure (XXIV) (cf. Bell *et al.*[1]).

Confimration of the molecular structures of some halogeno-2:7-dihydroxynaphthalenes by the preparation of quinones

From 2:7-dimethoxynaphthalene was obtained the yellow-orange 1:4-quinone, made by Fieser and Brown from ammonium 7-methoxy-1:2-naphthaquinone-4-sulphonate.[17]

The oxidation of the dibromo-2:7-dimethoxynaphthalene afforded a maroon and a yellow product. The colour of the former is indicative of an *o*-quinone, whilst that of the latter is characteristic of a *p*-quinone.[18] The analytical results for the maroon compound correspond to a dibromodimethoxynaphthaquinone, and the other compound appears to be a monobromodimethoxynaphthaquinone. Now these results are compatible with the representation of the dibromodiol by the formula (IV), but not by the formula (II). An *amphi*-quinone containing both of the methoxy groups is clearly impossible. Thus the products of oxidation have the structures (XVII) and (XVIII).



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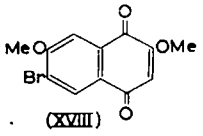
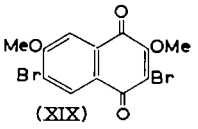


(XVIII)

The tribromo-2:7-dimethoxynaphthalene yielded a yellow quinone, isomeric with, but different from, the dibromoquinone (XVII) obtained by the oxidation of the dibromodimethoxynaphthalene. The sole reasonable structure for this new quinone

[15] J. Pollak and E. Gebauer-Fülnegg, *Anz. Akad. Wiss. Wien* **63**, 145 (1927); *Chem. Abstr.* **22**, 3651 (1928).
[16] J. Pollak and E. Gebauer-Fülnegg, *Mh. Chem.* **50**, 310 (1928).
[17] L. F. Fieser and R. H. Brown, *J. Amer. Chem. Soc.* **71**, 3615 (1949).
[18] E. Cerutti and J. Martinet, *C. R. Acad. Sci., Paris* **237**, 1336 (1953).

is given by the formula (XIX), which is consistent with attributing to the tribromo-2:7-dihydroxynaphthalene the formula (XVI), proposed both by Ioffe and Fedorova and by the present author. It is to be noted, however, that this structure is precisely that for the only possible dibromodimethoxynaphthaquinone from the oxidation of the dibromodimethoxynaphthalene corresponding to the structure (II) advocated by Ioffe and Fedorova for the dibromodiol.



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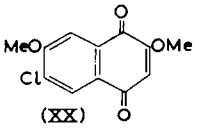
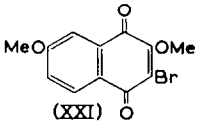
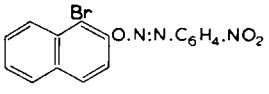


(XX)

From the oxidation of the dichloro-2:7-dimethoxynaphthalene has been isolated only a yellow compound, containing one atom of chlorine in its molecule. This product, from a consideration of the result of the oxidation of the bromo analogue, is given the formula (XX). Although it is true that the analytical results for this compound (XX) do not preclude the representation of the dichlorodiol by Clausius's formula (I),[19] this is opposed by the fact that the dibromodiol does not have the structure (II) and yet on dichlorination it yields the same compound as that obtained by the dibromination of the dichloro-2:7-dihydroxynaphthalene (see introduction to this paper).



(XXI)



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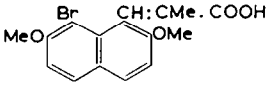
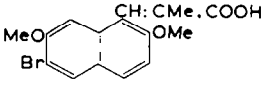


(XXIII)



(XXIV)

Note added in proof: The author has overlooked a communication by Cooke, Johnson and Owen,[20] who have submitted experimental evidence that the major product of the dibromination of 2:7-dihydroxynaphthalene is the 1:6-derivative (m.p. 162–163°). They have prepared also 3-bromo-2:7-dihydroxynaphthalene (m.p. 191–192°). The only monobromo-derivative that has previously been described[1,18] is 1-bromo-2:7-dihydroxynaphthalene (m.p. 135°), the structure of which is discussed above.

EXPERIMENTAL*

2:7-Dimethoxynaphthalene. This ether was prepared in the normal way, by shaking dimethyl sulphate with a solution of the diol in aqueous sodium hydroxide. Light

* Melting points are uncorrected for the emergent column.

[19] A. Clausius, *Ber. Dtsch. Chem. Ges.* **23**, 517 (1890).

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

cream-coloured needles, m.p. 138° (67 per cent of theoretical yield), were obtained by recrystallisation from acetic acid. A second crop of crystals (5 per cent of theoretical yield) melted at 135–136° (138°[21]).

2:7-*Dimethoxy*-1:4-*naphthaquinone*. To a solution (at 20°) of 2:7-dimethoxynaphthalene (5·51 g) in acetic acid (250 ml) was added in small portions during 3 hr, a solution (at 20°) of chromium trioxide (24·4 g) in water (53 ml). The heat of reaction gave a maximum temperature of 43° during the mixing. After being left for 24 hr, the product was heated to 40° for 30 min, cooled and poured into water (3·5 l.). The precipitate (1·31 g), after being washed with water and dried, melted at 212°. Crystallisation from acetic acid afforded small yellow-orange needles, m.p. 215° (Found: C, 65·7; H, 4·8. Calc. for $C_{12}H_{10}O_4$: C, 66·0; H, 4·6 per cent). Fieser and Brown,[17] who prepared this compound by a different method, recorded a m.p. of 214–215°.

3-*Bromo*-2:7-*dimethoxy*-1:4-*naphthaquinone* (XXI). A solution of bromine (0·16 ml) in acetic acid (25 ml) was added during 20 min to 2:7-dimethoxy-1:4-naphthaquinone (0·57 g) in the same solvent (13 ml). The mixture was then kept at 60–80° for 30 min before it was poured into water (500 ml). The precipitate (0·65 g) melted at 132–134°. Crystallisation from acetic acid gave minute orange needles of the *bromo derivative*, m.p. 136·5° (Found: C, 48·5; H, 3·1; Br, 26·8. $C_{12}H_9O_4Br$ requires C, 48·5; H, 3·1; Br, 26·9 per cent). The use of twice the above-mentioned proportion of bromine gave a smaller yield of 3-bromo-2:7-dimethoxy-1:4-naphthaquinone as the only isolable product. In connexion with the ascribed structure (XXI), it may be mentioned that treatment of 5:8-dihydroxy-1:4-naphthaquinone with bromine afforded the 2-bromo derivative.[22]

1:6-*Dibromo*-2:7-*dimethoxynaphthalene*. A solution of bromine (4·7 g) in acetic acid (10 ml) was poured into a solution of 2:7-dimethoxynaphthalene (2·60 g) in the same solvent (65 ml). After 24 hr the precipitated needles were filtered off and washed with acetic acid. The dry light-grey product (3·38 g) melted at 129–130° (131° in lit.[1], where the compound is designated as "2:7-dibromo-3:6-dimethoxynaphthalene").

Oxidation of 1:6-*dibromo*-2:7-*dimethoxynaphthalene*. A solution (at 15°) of chromium trioxide (2·27 g) in water (3·5 ml) was added to a solution (at 50°) of 1:6-dibromo-2:7-dimethoxynaphthalene (2·06 g) in acetic acid (50 ml). After 1 hr the mixture was poured into water (300 ml). After being washed with water and dried, the dark-red precipitate (0·60 g) was treated with acetic acid at 100°. Filtration of the hot product gave a maroon residue (A). From the cold filtrate was deposited a solid, which was filtered off and washed with acetic acid, to yield a yellow-brown residue (B).

The substance (A) was recrystallised from benzene, to give minute maroon needles of 4:7-*dibromo*-3:6 *dimethoxy*-1:2-*naphthaquinone* (XVII), m.p. 230° (Found: C, 38·6; H, 1·9. $C_{12}H_8O_4Br_2$ requires C, 38·3; H, 2·1 per cent).

Recrystallisation of the residue (B) from acetic acid furnished very small yellow needles of 6-*bromo*-2:7-*dimethoxy*-1:4-*naphthaquinone* (XVIII), m.p. 256–258° (Found: C, 47·9; H, 3·5; Br, 27·4. $C_{12}H_9O_4Br$ requires C, 48·5; H, 3·1; Br, 26·9 per cent).

An attempt was made to use *n*-butyric acid[23] as the solvent for oxidation by chromium trioxide, but the only compound isolated from the mixture was unchanged 1:6-dibromo-2:7-dimethoxynaphthalene.

[21] S. N. Chakravarti and V. Pasupati, *J. Chem. Soc.* 1859 (1937).
[22] L. Brüll and P. Girotti, *Ann. Chim. Appl.* **26**, 19 (1936).
[23] R. D. Wilson, *Chem. & Ind.* 758 (1957).

1:3:6-*Tribromo*-2:7-*dimethoxynaphthalene*. To a solution of 2:7-dimethoxynaphthalene (18·9 g) in acetic acid (600 ml) was added bromine (16·3 ml) in acetic acid (200 ml) in small portions during 50 min. The mixture was then kept at 100° for 2 hr. Cooling and subsequent filtration yielded light-grey needles (15·7 g), m.p. 164–167°. Dilution of the mother-liquor with water (1 l.) precipitated more solid (22 g; greenish brown).

The solid with m.p. of 164–167° was recrystallised from acetic acid and then from ethanol, to give minute white needles, m.p. 172·5°. 1:3:6-Tribromo-2:7-dimethoxynaphthalene, prepared by methylating the tribromodiol, melted[1] at 173°.

2:7-*Dibromo*-3:6-*dimethoxy*-1:4-*naphthaquinone* (XIX). To 1:3:6-tribromo-2:7-dimethoxynaphthalene (5·55 g) in acetic acid (200 ml) was slowly added, in small portions, a solution of chromium trioxide (10·5 g) in water (23 ml). The maximum temperature of the product during the mixing was 22°. The mixture was then kept at 50° for 1 hr, cooled and filtered, to give a grey residue (0·5 g). The filtrate was poured into water (1·5 l.) to yield a precipitate, from which, by repeated crystallisation from acetic acid, were obtained very small yellow needles of 2:7-*dibromo*-3:6-*dimethoxy*-1:4-*naphthaquinone* (XIX), m.p. 212·5–213·5° (Found: C, 38·5; H, 2·0. $C_{12}H_8O_4Br_2$ requires C, 38·3; H, 2·1 per cent).

The use of one-half of the above proportion of chromium trioxide afforded a considerable yield of unchanged tribromodimethoxynaphthalene, while attempted oxidation with potassium permanganate in AnalaR acetone led to the recovery of 87 per cent of the original tribromodimethoxynaphthalene.

1:6-*Dichloro*-2:7-*dimethoxynaphthalene*. Sulphuryl chloride (5·7 ml) was added cautiously to 2:7-dimethoxynaphthalene (6·1 g) in chloroform (10 ml). The mixture was heated under reflux for 30 min, cooled and filtered. Concentration of the filtrate yielded a dark brown substance, which was discarded. The residue, after being washed with a small quantity of chloroform, weighed 3·4 g and melted at 140–143°. Recrystallisation from acetic acid gave white prisms of 1:6-*dichloro*-2:7-*dimethoxynaphthalene*, m.p. 143–143·5° (Found: C, 56·9; H, 4·1; Cl, 27·2. $C_{12}H_{10}O_2Cl_2$ requires C, 56·1; H, 3·9; Cl, 27·6 per cent).

6-*Chloro*-2:7-*dimethoxy*-1:4-*naphthaquinone* (XX). A solution (at 15°) of chromium trioxide (5·5 g) in water (14 ml) was run, during 5 min, into 1:6-dichloro-2:7-dimethoxynaphthalene (2·82 g) in acetic acid (70 ml) at 50°. After 1 hr the product was diluted with water (700 ml). The isolated precipitate (0·41 g) was recrystallised twice from a filtered solution in hot acetic acid. Sublimation of the product afforded yellow-orange needles of 6-*chloro*-2:7-*dimethoxy*-1:4-*naphthaquinone* (XX), m.p. 280–282° (Found: C, 56·6, 56·6; H, 3·6, 3·5; Cl, 14·4. $C_{12}H_9O_4Cl$ requires C, 57·0; H, 3·6; Cl, 14·0 per cent).