600. *Halogenation of Naphthalene-2,7-diol*

By R. D. Wilson

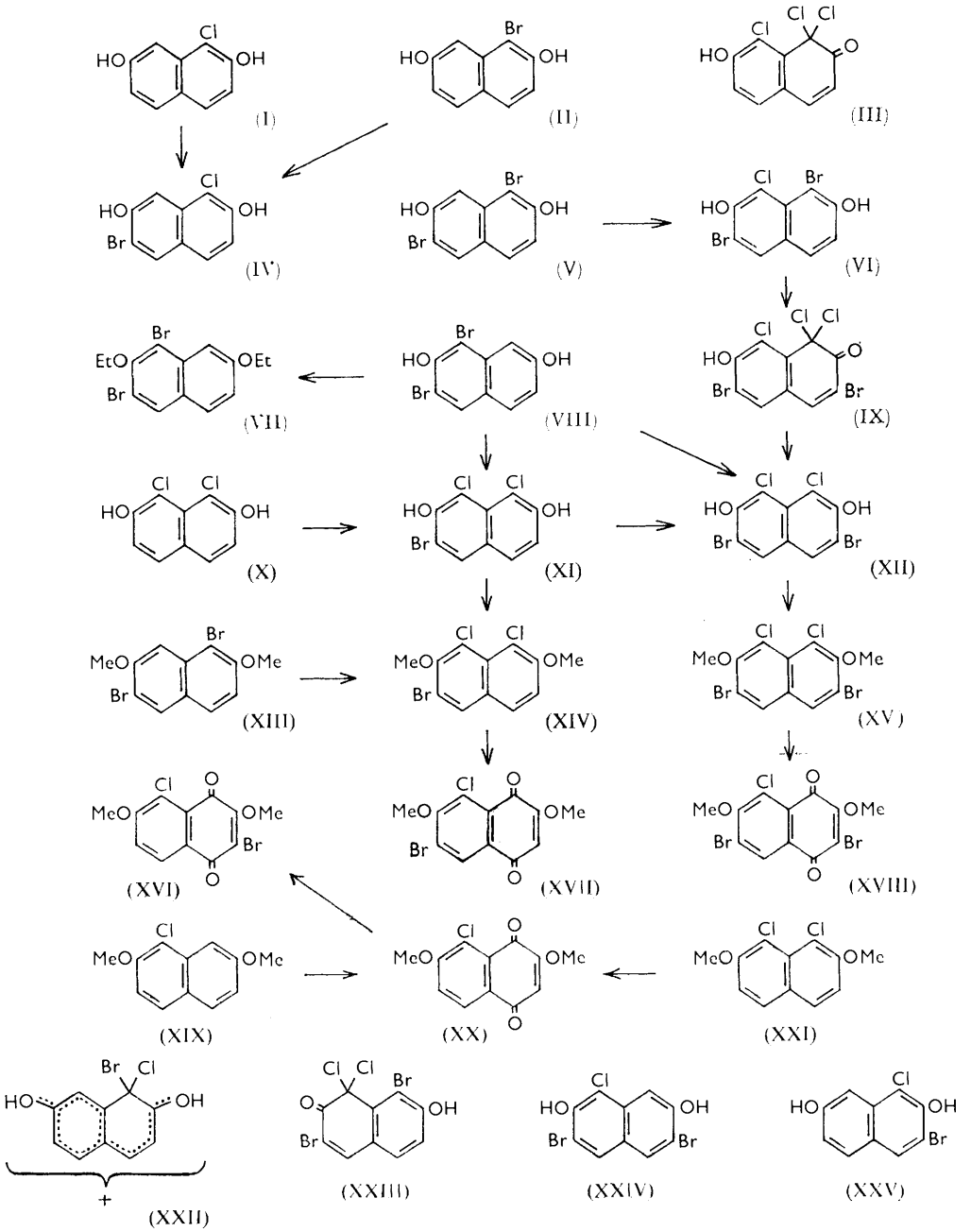
6-Bromo-1-chloronaphthalene-2,7-diol has been obtained by bromination of 1-chloro- and by chlorination of 1-bromo-naphthalene-2,7-diol. It has been confirmed that dichlorination of naphthalene-2,7-diol gives the 1,8-derivative. Whereas mono- and di-bromination of 1,8-dichloronaphthalene-2,7-diol gave, respectively, the 3- and 3,6-derivatives, chlorination of 1,6-dibromonaphthalene-2,7-diol gave the 8-chloro-derivative and 3,6-dibromo-1,8,8-trichloro-7,8-dihydro-7-oxo-2-naphthol. 3-Bromo-1,8-dichloro- and 3,6-dibromo-1,8-dichloro-naphthalene-2,7-diol were formed by the chlorination of 1,3-dibromonaphthalene-2,7-diol. 3-Bromo-1,8-dichloro-2,7-dimethoxynaphthalene arose by methylation of the corresponding phenol and by chlorination of 1,6-dibromo-2,7-dimethoxynaphthalene. Some mechanistic implications of these results are discussed.

The preparation of tetrabromonaphthalene-2,7-diol has been repeated; an explanation is offered for the reported failure to prepare this compound.

The orientations of some halogeno-derivatives of naphthalene-2,7-diol are considered in relation to the established molecular structures of products of its bromination [1-3] [1-bromo- (II), 1,3- (VIII) and 1,6-dibromo- (V), and 1,3,6-tribromo-naphthalene-2,7-diol (XXXI)] and of its chlorination [1-chloro- (I) (see Experimental section) and 1,8-dichloro-naphthalene-2,7-diol (X) [4]]. Oxidation of the ethers (XIX) and (XXI) gave the same chloro-1,4-naphthaquinone, which must have the formula (XX); this confirms the structure assigned to the dichloro-diol (X) by Bell.[4]

[1] R. D. Wilson, *Tetrahedron*, 1958, **3**, 236.
[2] R. D. Wilson, *Tetrahedron*, 1960, **11**, 256.
[3] R. G. Cooke, B. L. Johnson, and W. R. Owen, *Austral. J. Chem.*, 1960, **13**, 256.
[4] F. Bell, *J.*, 1961, 5293.

The 1-chloro-derivative (I), made from naphthalene-2,7-diol by reaction with *N*-chlorosuccinimide, was monobrominated to give a compound identical with that obtained by chlorination of the 1-bromo-diol (II). The product of the two reactions was shown to be



6-bromo-1-chloronaphthalene-2,7-diol (IV) by the similarity of its infrared spectrogram to that [5] of 1,6-dibromonaphthalene-2,7-diol (V) and by its difference from that of the 1,8-dichloro-diol (X). This orientation of the bromochloro-diol (IV) is analogous to those

[5] Sadtler spectrogram, no. 18,866.

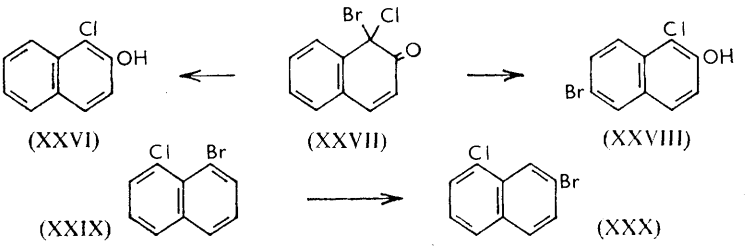
of the corresponding dimethyl [4] and diethyl [6] ethers, and, in the product from the 1-bromo-diol (II), probably results from the displacement of the bromo-substituent and its heteronuclear migration. An intermediate cation (XXII), of the type suggested by Bell and Buck,[6] is considered to be formed. Although the migration may involve an intermolecular or intramolecular mechanism,[7] the hydroxy-substituents favour the latter. The entry of the displaced bromine into the chlorine-free ring, to form the compound (IV), is explained by an inductive effect, whilst the absence of *peri*-substitution is mainly a steric consequence [contrast the production of the 1,8-dichloro-diol (X)]. The rupture of the bond to bromine rather than the one to chlorine in the intermediate is a result of their relative strengths.[8] In this connection, Fries and Schimmelschmidt [9] have shown that 1-bromo-1-chloro-2-naphthone (XXVII) is reduced to 1-chloro-2-naphthol (XXVI) and is transformed into 6-bromo-1-chloro-2-naphthol (XXVIII) by hydrogen bromide or hydrogen chloride. Further, Koptyug *et al.*[10] isomerised 1-bromo-8-chloronaphthalene (XXIX), in the presence of naphthalene-2-sulphonic acid, into 7-bromo-1-chloronaphthalene (XXX).

1,8-Dichloronaphthalene-2,7-diol (X) was brominated smoothly in stages, to yield the compounds (XI) and (XII). The spectrogram of the former product showed significant differences from that [11] of the 1,3,6-tribromo-diol (XXXI). The *peri*-substituents of the 1,8-dichloro-diol probably exhibit both lateral and out-of-plane displacements,[12] but Courtauld atomic models indicate that in this compound, buttressing [13] would not interfere with substitution by bromine at the 3- and 6-positions.

Despite the migration of bromine during the chlorination of 1-bromonaphthalene-2,7-diol (II), the reaction between one molar proportion of sulphuryl chloride and the 1,6-dibromo-diol (V) yielded the 8-chloro-derivative (VI). [In this Paper "1,6-dibromonaphthalene-2,7-diol" and "crude dibromonaphthalene-2,7-diol" (and equivalent terms in each case) refer, respectively, to the pure isomer isolated by chromatography [2,3] and to the mixture of *ca.* 70% of 1,6- (V) and 30% of 1,3-dibromonaphthalene-2,7-diol (VIII) obtained directly by bromination.[3]] The structure (VI) assigned to the dibromochloro-compound is justified by a comparison of the spectrogram with those of the bromodichloro-diol (XI) and the tribromo-diol (XXXI).[11] Several attempts to introduce, by direct halogenation with chlorine or sulphuryl chloride, more than one chloro-substituent into the 1,6-dibromo-diol led to the isolation of the compounds (VI) and (IX). In view of the result of monochlorination of 1-bromonaphthalene-2,7-diol (II), this result may be related to the difficulty in effecting the migration of bromine from the 1-position of the 1,6-dibromo-diol, by way of an intermediate analogous to the cation (XXII), to the sterically hindered 8-position of the ring which already bears an inductively adverse bromo-substituent. The sole remaining site to which the bromine may migrate involves the 3-carbon atom of the intermediate formed from the 1,6-dibromo-diol, which would be in the ring substituted by the displacing chlorine. Such a migration appears to be possible only under severe chlorinating conditions (*e.g.*, when three molar proportions of sulphuryl chloride are used), when the product isolated is the quinolide (recently defined [14]) compound (IX). Under mild conditions direct attack by the chlorinating reagent at the 8-position of the 1,6-dibromo-diol (V) occurs instead of displacement of the 1-bromo-substituent. As the dibromodichloro-diol (XII) was not obtained by chlorination of the

[6] F. Bell and K. R. Buck, *J.*, 1963, 6069.
[7] M. J. S. Dewar, "Molecular Rearrangements," vol. 1, ed. P. de Mayo, Wiley, New York, 1963, p. 305.
[8] T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 2nd edn., 1958, p. 203 *et seq.*
[9] K. Fries and K. Schimmelschmidt, *Annalen*, 1930, **484**, 245.
[10] V. A. Koptyug, V. A. Plakhov, and V. G. Shubin, *Zhur. obshchei Khim.*, 1961, **31**, 4023.
[11] Sadtler spectrogram, no. 18,867.
[12] O. Bastiansen and O. Hassel, *Acta Chem. Scand.*, 1947, **1**, 489.
[13] F. H. Westheimer, "Steric Effects in Organic Chemistry," ed. M. S. Newman, Wiley, New York, 1956, p. 552.
[14] G. N. Bogdanov, V. V. Ershov, and A. A. Volod'kin, *Russ. Chem. Rev.*, 1963, **32**, 75.

1,6-dibromo-diol (V) [contrast the behaviour of the 1,3-isomer (VIII) in the mixture of the two dibromo-diols described in the present work], it seems that the formation of the quinolide compound (XXIII) (in which the steric strain in the *peri*-positions is relieved) *via* the dibromochloro-diol (VI) may precede displacement with migration, to give the



compound (IX). The formation of the compound (IX) reflects the relative stability of such keto-structures in the naphthalene series [15] and is consistent with the high yield of 1,8,8-trichloro-7,8-dihydro-7-oxo-2-naphthol (III) obtainable by the chlorination of naphthalene-2,7-diol with 3·7 molar proportions of sulphuryl chloride.[4]

The crude product obtained by dibromination of naphthalene-2,7-diol [*i.e.*, a mixture of compounds (V) and (VIII)] was treated with three molar proportions of sulphuryl chloride to give, besides the compound (IX), small yields of 3-bromo-1,8-dichloro- and 3,6-dibromo-1,8-dichloro-naphthalene-2,7-diol (XI and XII, respectively); the former product was also made by the use of molecular chlorine. The precursor of these two compounds is considered to be 1,3-dibromonaphthalene-2,7-diol (VIII), as they have not been obtained by similar chlorinations of the pure 1,6-dibromo-2,7-diol (V). The intermediate [cf. the cation (XXII)] from the 1,3-dibromo-diol would contain a bromine-free ring, and so the migration of bromine from the α-position could occur by a process analogous to that which occurs during the chlorination of the 1-bromo-diol (II), to give the compound (XXIV). Chlorination of the last compound would account for the formation of the dibromodichloro-diol (XII). However, some of the intermediate cation appears to have lost bromine and formed the bromodichloro-diol (XI), *via* the compound (XXV). In a previous Paper on the chlorination of crude dibromonaphthalene-2,7-diol,[16] published before the occurrence of the 1,3-dibromo-diol (VIII) in the product of dibromination of naphthalene-2,7-diol was established, the implied source of the dibromodichloro-derivative (XII) was incorrect. When the pure 1,6-isomer (V) reacted with sulphuryl chloride under the conditions of the earlier experiment,[16] only the dibromochloro-diol (VI) was isolated, although in the light of other results of the present work, the mother-liquor would have probably yielded the quinolide compound (IX). The dibromodichloro-diol (XII) was alternatively prepared, apparently *via* the derivative (IX), by reduction, with zinc and acetic acid, of a product obtained by chlorination of 1,6-dibromonaphthalene-2,7-diol.[16] Reduction of the material from the chlorination of crude dibromo-diol led to the isolation of the bromodichloro-diol (XI) in a yield compatible with its formation from the 1,3-dibromo-diol (VIII). The oxidation of the dimethyl ether (XV) was repeated, and gave the pure quinone (XVIII). The impurity in the quinone prepared previously [16] is thought, in view of recent work,[2] to have been a carboxylic acid. The analytical results are consonant with this conclusion.

The chlorination of 1,6-dibromo-2,7-dimethoxynaphthalene (XIII) (see ref. 3 with regard to the absence of the 1,3-isomer) with 2·6 molar proportions of sulphuryl chloride afforded a fair yield of 3-bromo-1,8-dichloro-2,7-dimethoxynaphthalene (XIV). The difference between the behaviour of the ether (XIII) and the parent phenol (V) is ascribed chiefly to the impossibility of the formation of a relatively stable quinolide structure [17] by

[15] R. H. Thomson, *Quart. Rev.*, 1956, **10**, 32; L. Cannell, *J. Amer. Chem. Soc.*, 1957, **79**, 2932; G. O. Dudek, *ibid.*, 1963, **85**, 694; P. F. Holt and C. J. McNae, *J.*, 1964, 1759.

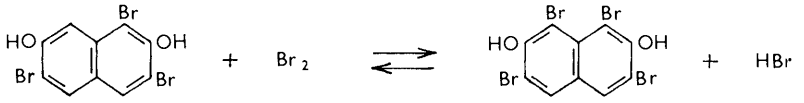
[16] F. Bell, J. A. Gibson, and R. D. Wilson, *J.*, 1956, 2335.

[17] J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, 2nd edn., 1962, p. 110.

the ether. Presumably the displaced α-bromo-substituent does not return to the ring in the available β-position because of steric hindrance offered by the methoxyl group.[18]

Oxidation of 3-bromo-1,8-dichloro-2,7-dimethoxynaphthalene (XIV) with chromic acid gave 6-bromo-8-chloro-2,7-dimethoxy-1,4-naphthaquinone (XVII). The structure of this quinone was proved by the unambiguous preparation of the alternative isomer (XVI) by bromination of the chloronaphthaquinone (XX) (cf. the production of 2-bromo-3,6-dimethoxy-1,4-naphthaquinone from the bromine-free quinone [1]).

The tetrabromonaphthalene-2,7-diol (XXXII) has been prepared by bromination of



(XXXI) (XXXII)

the tribromo-diol (XXXI). The failure of Cooke *et al.*[3] and of Ioffe and Fedorova [19] to make this compound by direct halogenation may be related to the mobility, in the presence of hydrogen halide, of an α-halogeno-substituent.[2-4,20] It seems that the equilibrium (XXXI ⇌ XXXII) may have arisen, and that under their conditions it was unfavourable for the existence of an appreciable proportion of the tetrabromo-diol. In a similar way may be explained Bell's success in repeating the preparation of the corresponding dimethyl ether,[4,16] which contrasts with others' inability to isolate this compound after the use of more vigorous conditions.[3] As to the structure of the tetrabromo-diol,[6] the considerable resemblance of its spectrogram to that of the dibromodichloro-diol (XII) appears to be compatible with the same orientation of the halogeno-substituents in the two molecules.

Experimental

Melting points are corrected. Infrared spectrograms were made with potassium bromide discs in a Grubb–Parsons double-beam grating spectrophotometer.

1-*Chloronaphthalene*-2,7-*diol* (I).—*N*-Chlorosuccinimide [21] (17 g.) in pyridine (100 ml.) was added to naphthalene-2,7-diol (20 g.) in the same solvent (100 ml.). The mixture was left for 70 min., heated to 75°, cooled to 48° during 50 min., and then treated with 5N-hydrochloric acid (600 ml.). The resultant mixture was extracted with chloroform (5 × 140 ml.) and then with diethyl ether (8 × 300 ml.). The chloroform extract was dried and evaporated to give impure 1,8-dichloronaphthalene-2-7-diol (X), which was crystallised from acetic acid and from isobutyl alcohol (charcoal) to give purer material (0·51 g.), m. p. and mixed m. p. with an authentic sample 187—189° (lit.,[16] 189°), mixed m. p. with naphthalene-2,7-diol 156—159°. The ether extract was dried and evaporated, and the residue was crystallised from acetic acid (charcoal) to give the 1-*chloro-diol* (7·8 g.), m. p. 170° after recrystallisation as needles from toluene (Found: C, 61·4; H, 3·5; Cl, 18·0. $C_{10}H_7ClO_2$ requires C, 61·7; H, 3·6; Cl, 18·2%).

Oxidation of 1,8-*Dichloro*-2,7-*dimethoxynaphthalene* (XXI).—To the dichloro-compound (100 g.; m. p. 143·5—145°; prepared in 79% yield from 2,7-dimethoxynaphthalene; [1] previously designated [1,2] as the 1,6-dichloro-ether) in acetic acid (1·5 l.) was added, during 3 hr., AnalaR chromium trioxide (311 g.) in water (310 ml.) (maximum temperature 52°). The mixture was kept for 16 hr. and then diluted with water (11 l.). The precipitate was washed with aqueous sodium hydrogen carbonate and crystallised from acetic acid to give deep yellow needles of 5-*chloro*-3,6-*dimethoxy*-1,4-*naphthaquinone* (XX) (5·6 g.), m. p. 292—293° (sublimed) (Found: C, 57·3; H, 3·6; Cl, 14·1. $C_{12}H_9ClO_4$ requires C, 57·0; H, 3·6; Cl, 14·0%); $\nu_{max.}$ 707w, 741, 776w, 843s, 870w, 880w, 901w, 950, 1025s, 1090s, 1125, 1150s, 1175s, 1195s, 1245vs, 1280vs, 1305, 1345vs, 1405, 1435s, 1470, 1565s, 1615s, 1640s, and 1680s cm.$^{-1}$. Earlier [1] this compound

[18] P. P. Shorygin and Z. S. Egorova, *Doklady Akad. Nauk S.S.S.R.*, 1958, **121**, 869; R. J. W. Le Fèvre and A. Sundaram, *J.*, 1962, 4756.
[19] I. S. Ioffe and N. M. Fedorova, *Zhur. obshchei Khim.*, 1936, **6**, 1079.
[20] S. Kura, S. Tanaka, and M. Tomita, *J. Pharm. Soc. Japan*, 1956, **76**, 1122.
[21] T. H. Chao and L. P. Cipriani, *J. Org. Chem.*, 1961, **26**, 1079; J. C. Martin and R. E. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 354.

was wrongly described as " 6-chloro-2,7-dimethoxy-1,4-naphthaquinone." Its spectrogram closely resembles that of the bromo-analogue [22] and differs from that of 6-bromo-2,7-dimethoxy-1,4-naphthaquinone.[2,23] With concentrated sulphuric acid the compound (XX) gave a deep purple colour.

Oxidation of 1-*Chloro*-2,7-*dimethoxynaphthalene* (XIX).—This compound [1·5 g.; m. p. 51—55° (lit.,[24] 58—60°)] was prepared from the diol (I) (2·3 g.) by treatment with aqueous sodium hydroxide and dimethyl sulphate (17 hr.; 15°), and oxidised as above. The crude product was washed with aqueous sodium hydrogen carbonate and with chloroform to leave the quinone (XX) (0·06 g.), identified by its m. p. and spectrogram.

1-*Bromonaphthalene*-2,7-*diol* (II).—Bromine (3·6 ml.) in chloroform (2·0 l.) was added during 4·5 hr. to a stirred solution of naphthalene-2,7-diol (10·8 g.) in chloroform (1·0 l.). The mixture was concentrated to 120 ml. and then filtered. The solid material was crystallised from 50% aqueous methanol (active carbon), to give the bromo-diol (8·1 g.), m. p. 138° (lit.,[3] 134—135°) unchanged by further recrystallisation from chloroform and from toluene (Found: C, 49·9; H, 2·8; Br, 32·5. Calc. for $C_{10}H_7BrO_2$: C, 50·2; H, 3·0; Br, 33·4%).

6-*Bromo*-1-*chloronaphthalene*-2,7-*diol* (IV).—(*a*) Bromine (1·62 ml.) in chloroform (100 ml.) was added during 1 hr. to 1-chloronaphthalene-2,7-diol (I) (5·89 g.) in the same solvent (300 ml.). The mixture was kept at 60° for 15 min., and then cooled and filtered to remove unchanged chloro-diol (0·27 g.). The solvent was removed from the filtrate, and the residue was crystallised from toluene (active carbon), to yield 6-*bromo*-1-*chloronaphthalene*-2,7-*diol* (1·5 g.), m. p. 201° (sublimed) (Found: C, 44·0, 43·9; H, 2·9, 2·4; Br, 29·3; Cl, 12·8. $C_{10}H_6BrClO_2$ requires C, 43·9; H, 2·2; Br, 29·2; Cl, 13·0%); $\nu_{max.}$ 690w, 745w, 761w, 803, 844, 858, 870s, 990, 1030, 1135s, 1155vs, 1215s, 1245, 1265, 1280, 1305w, 1335, 1370s, 1440, 1455, 1500s, 1565w, 1590, 1620, 3345s, and 3470s cm.$^{-1}$. A similar spectrogram was given by 1,6-dibromonaphthalene-2,7-diol (V),[5] but that of the dichloro-diol (X) was markedly different (see below).

(*b*) To 1-bromonaphthalene-2,7-diol (II) (3·54 g.) in chloroform (150 ml.) was added sulphuryl chloride (1·25 ml.) in the same solvent (32 ml.). After 1 hr. the mixture was kept at 55° for 70 min., and then the solvent was removed. The residue was crystallised from toluene (active carbon) and chromatographed in a 2 : 2 : 1 mixture of benzene, chloroform, and methanol on silica gel. After development (benzene) the brown band was extruded and extracted with methanol. The product was crystallised from toluene (active carbon) to give the acircular bromochloro-diol (IV) (0·10 g.), m. p. 197—198° after a further recrystallisation (Found: C, 43·5; H, 1·8; Br, 29·2%). A mixed m. p. with the sample prepared by method (*a*) was 197·5—199·5°.

3-*Bromo*-1,8-*dichloronaphthalene*-2,7-*diol* (XI).—1,8-Dichloronaphthalene-2,7-diol (X), m. p. 190·5—192°, was prepared by Bell's method [4] (Found: C, 52·8; H, 3·0. Calc. for $C_{10}H_6Cl_2O_2$: C, 52·4; H, 2·6%); $\nu_{max.}$ 722w, 761w, 824, 831s, 891, 1040w, 1135sh, 1140s, 1175vs, 1215vs, 1265w, 1325, 1345s, 1370w, 1435s, 1515, 1555w, 1610s, 3355s, and 3380sh cm.$^{-1}$. Bromine (3·2 ml.) in acetic acid (48 ml.) was added to a solution (42°) of the dichloro-diol (14·0 g.) in the same solvent (330 ml.). After 2 hr. the mixture was filtered, and the solid was crystallised from acetic acid and from toluene (charcoal) to give faintly orange-pink needles of 3-*bromo*-1,8-*dichloronaphthalene*-2,7-*diol* (XI) (1·8 g.), m. p. 199° (decomp.) (Found: C, 39·1; H, 1·8; Br, 26·0; Cl, 22·8. $C_{10}H_5BrCl_2O_2$ requires C, 39·0; H, 1·6; Br, 25·9; Cl, 23·0%); $\nu_{max.}$ 621, 735w, 754w, 768w, 801, 828, 876, 908w, 1020, 1060, 1160vs, 1210s, 1235, 1295sh, 1305, 1355s, 1420s, 1450w, 1500, 1545, 1595sh, 1615s, 3425s, and 3460s cm.$^{-1}$. The filtrate afforded more bromodichloro-diol (XI) (4·6 g.). The m. p. and colour of the compound were unaltered by storage in the dark for 2 years.

3-*Bromo*-1,8-*dichloro*-2,7-*dimethoxynaphthalene* (XIV).—(*a*) The preceding bromodichloro-diol (1·70 g.) was methylated (dimethyl sulphate and aqueous sodium hydroxide), to give the *dimethyl ether* (0·91 g.) as needles, m. p. 131° after crystallisation (active carbon) from light petroleum (b. p. 60—80°) (Found: C, 42·8; H, 2·8; Br, 23·5; Cl, 21·2; OMe, 18·4. $C_{12}H_9BrCl_2O_2$ requires C, 42·9; H, 2·7; Br, 23·8; Cl, 21·1; 2 OMe, 18·5%); $\nu_{max.}$ 556w, 620w, 636, 708w, 729w, 760, 773, 791, 877, 912, 950, 998s, 1045s, 1095s, 1155w, 1170w, 1195, 1235s, 1255s, 1290s, 1330vs, 1345sh, 1385, 1410w, 1450, 1490s, 1525, 1580, and 1610 cm.$^{-1}$.

(*b*) 1,6-Dibromo-2,7-dimethoxynaphthalene (XIII) [1,3] (4·7 g.) in chloroform (100 ml.) was treated with sulphuryl chloride (1·1 ml.) in the same solvent (20 ml.). After 40 min. a further

[22] Sadtler spectrogram, no. 18,865.
[23] Sadtler spectrogram, no. 18,864.
[24] F. Bell and J. R. Gorrie, *J.*, 1961, 4258.

portion of sulphuryl chloride (1·8 ml.) in chloroform (15 ml.) was added. The mixture was kept for 50 min. and then the volatile material was removed by distillation. The residue was washed with water and crystallised from acetic acid (active carbon) and from light petroleum (b. p. 60—80°), to give the dimethyl ether (1·1 g.), m. p. 127·5—128·5° raised to 130° by further crystallisations from light petroleum and from n-propanol (Found: C, 42·5; H, 2·3; OMe, 18·3%). This compound was identical (mixed m. p. and spectrograms) with the product obtained by methylation of the bromodichloro-diol (XI).

Oxidation of 3-*Bromo*-1,8-*dichloro*-2,7-*dimethoxynaphthalene* (XIV).—To this compound [1·7 g.; from the ether (XIII)] in acetic acid (250 ml.) was added AnalaR chromium trioxide (6·2 g.) in water (26 ml.). After 15 min. the mixture was diluted with water (2·0 l.) and the precipitate was washed with aqueous sodium hydrogen carbonate and chromatographed in chloroform on alumina. The solid isolated from the yellow band was crystallised from acetic acid (or n-propanol) to give pale yellow needles of 6-*bromo*-8-*chloro*-2,7-*dimethoxy*-1,4-*naphthaquinone* (XVII) (0·14 g.), m. p. 206° (sublimed) (Found: C, 43·8; H, 2·35; Br, 24·3; Cl, 10·5. $C_{12}H_8BrClO_4$ requires C, 43·5; H, 2·4; Br, 24·1; Cl, 10·7%).

A similar yield of the same quinone (mixed m. p.) was furnished by oxidation of the bromodichloro-ether obtained by methylation of the corresponding phenol (XI), which had been derived from 1,8-dichloronaphthalene-2,7-diol (X). This result further confirms the identity of the bromodichloro-ethers from the two sources.

3,6-*Dibromo*-1,8-*dichloronaphthalene*-2,7-*diol* (XII).—Into the 3-bromo-1,8-dichloro-2,7-diol (XI) (5·1 g.) and sodium acetate trihydrate (6·8 g.) in acetic acid (230 ml.) at 40° was poured bromine (0·87 ml.) in acetic acid (20 ml.). After 1·5 hr. the mixture was filtered to give the acircular dibromodichloro-diol (2·0 g.), m. p. 211° raised to 213° (decomp.; sublimed) by crystallisation from toluene active carbon (lit.,[16] 204—205°) (Found: C, 31·0; H, 0·9; Br, 41·3; Cl, 18·0. Calc. for $C_{10}H_4Br_2Cl_2O_2$: C, 31·0; H, 1·0; Br, 41·3; Cl, 18·3%); $\nu_{max.}$ 442, 540w, 559, 644w, 658, 662sh, 749w, 786w, 832, 882, 898, 933w, 1045, 1070w, 1125w, 1175vs, 1200s, 1240, 1280w, 1310s, 1355s, 1410s, 1445, 1495, 1545, 1590w, 1605, 3065w, 3450s, 3495, and 3570 cm.$^{-1}$. The filtrate afforded a further crop (0·4 g.) of the same product. The colour and m. p. had not changed after 15 months in the dark.

Oxidation of 3,6-*Dibromo*-1,8-*dichloro*-2,7-*dimethoxynaphthalene* (XV).—This ether had m. p. 149° (from n-propanol) (lit.,[16] 150°) (Found: C, 35·1; H, 2·1; Br, 37·7; Cl, 17·1; OMe, 14·6. Calc. for $C_{12}H_8Br_2Cl_2O_2$: C, 34·7; H, 1·9; Br, 38·5; Cl, 17·1; 2 OMe, 15·0%); $\nu_{max.}$ 555, 651, 667w, 682, 762, 782, 891s, 927, 955s, 986s, 1070s, 1180w, 1225s, 1235s, 1330vs, 1370, 1395, 1425, 1465s, 1510s, 1565w, and 1580w cm.$^{-1}$. It (0·18 g.) was oxidised [16] and the product was washed with aqueous sodium hydrogen carbonate to give the *quinone* (XVIII) (0·08 g.), m. p. 161·5—162·5° raised to 164° by crystallisation from n-propanol (Found: C, 35·3; H, 1·9; Br, 38·0. $C_{12}H_7Br_2ClO_4$ requires C, 35·1; H, 1·7; Br, 38·9%).

2-*Bromo*-5-*chloro*-3,6-*dimethoxy*-1,4-*naphthaquinone* (XVI).—A mixture of 5-chloro-3,6-dimethoxy-1,4-naphthaquinone (XX) (4·5 g.), sodium acetate trihydrate (7·8 g.), acetic acid (650 ml.), and bromine (1·7 ml.) was refluxed for 2 hr. and then, with more bromine (0·5 ml.) in acetic acid (30 ml.), for 1 hr. The precipitate obtained by diluting the mixture to 2 l. with water was chromatographed (alumina, chloroform), and the orange-yellow band afforded the *quinone* (XVI) (2·2 g.) as deep yellow prisms, m. p. 182·5—184° (from acetic acid) (Found: C, 44·0; H, 2·6; Br, 23·8; Cl, 10·7. $C_{12}H_8BrClO_4$ requires C, 43·5; H, 2·4; Br, 24·1; Cl, 10·7%).

Attempts to prepare the compound (XVI) by chlorination of 2-bromo-3,6-dimethoxy-1,4-naphthaquinone were unsuccessful. To ensure a good yield (83%) of the latter quinone from 2,7-dimethoxy-1,4-naphthaquinone, the process outlined earlier [1] was modified by keeping the mixture during bromination at 85° for 1 hr.

1,6-*Dibromo*-8-*chloronaphthalene*-2,7-*diol* (VI).—Sulphuryl chloride (0·48 ml.) in chloroform (7 ml.) was added to 1,6-dibromonaphthalene-2,7-diol [2,3] (V) (1·8 g.) in the same solvent (46 ml.) at 44°. The precipitate formed after 2·5 hr. was crystallised from toluene or n-propanol, to give white needles of the *dibromochloro-diol* (0·7 g.), m. p. 192° (decomp.) (Found: C, 34·1, 34·3; H, 1·7, 1·6; Br, 44·8, 46·3; Cl, 10·0, 9·9. $C_{10}H_5Br_2ClO_2$ requires C, 34·1; H, 1·4; Br, 45·3; Cl, 10·1%); $\nu_{max.}$ 724w, 751w, 768w, 803, 824, 861, 887w, 1010w, 1055, 1160vs, 1210, 1235, 1300, 1350s, 1380w, 1420s, 1455w, 1500, 1540, 1595, 1610, 2915w, 3065w, and 3425s cm.$^{-1}$.

Further Experiments on the Chlorination of 1,6-*Dibromonaphthalene*-2,7-*diol* (V).—Several attempts were made to introduce more than one chlorine atom into the 1,6-dibromo-diol by the use of chlorine or sulphuryl chloride. These yielded only the dibromochloro-diol (VI),

except where the use of higher proportions of chlorinating agent made the quinolide compound (IX) isolable. Three of the experiments are outlined below:

(*a*) When the conditions used earlier [16] for the preparation of the dibromodichloro-diol (XII) from the crude dibromo-diol [mixture of compounds (V) and (VIII) [3]] were applied to the pure 1,6-dibromo-diol (V) (9·3 g.), the dibromochloro-diol (VI) (4·3 g.) was isolated.

(*b*) 1,6-Dibromo-8-chloronaphthalene-2,7-diol (VI) (3·7 g.) in chloroform was left with sulphuryl chloride (2 molar proportions) for 1 week. The mixture was degassed by reduction of the pressure to 6 cm. Hg and then concentrated at this pressure and at 48° to 12 ml. Filtration yielded the dibromochloro-diol (VI) (2·0 g.), m. p. and mixed m. p. with an authentic sample 188° (Found: C, 34·9; H, 0·8%). The mother-liquor afforded the compound (IX) (0·24 g.), m. p. 163—164° (lit.,[16] 166°) which was identical (mixed m. p.) with the product of the next experiment.

(*c*) Chlorine (2 molar proportions) was passed into the dibromochloro-diol (VI) (4·3 g.) in acetic acid (80 ml.) at 42°. Water (220 ml.) was added, and the precipitate was crystallised from acetic acid to give compound (IX) (3·1 g.). This did not depress the m. p. of the penta-halogeno-compound made by chlorination of crude dibromonaphthalene-2,7-diol.[16]

Reaction of 3 *Molar Proportions of Sulphuryl Chloride with Crude Dibromonaphthalene-2,7-diol* [*Compounds* (V) *and* (VIII)] *and with Pure* 1,6-*Dibromonaphthalene-2,7-diol* (V).—Sulphuryl chloride (36 ml.) in chloroform (120 ml.) was added to crude dibromonaphthalene-2,7-diol (47 g.) in the same solvent (950 ml.). The product was kept at 50° for 40 min. and at 18° for 4 days, and then filtered. The solid was crystallised from toluene to give 3-bromo-1,8-dichloronaphthalene-2,7-diol (XI) (4 g.), m. p. 201° (Found: C, 38·6; H, 1·9%), which was identical (spectrograms) with a sample prepared by monobromination of the 1,8-dichloro-diol (X). Methylation of the product yielded the ether (XIV), m. p. 130—130·5° (Found: C, 42·8; H, 2·9; Br, 24·6; Cl, 21·4; OMe, 18·5%), which was identical (spectrograms) with a sample prepared by monobromination of the 1,8-dichloro-diol, and methylation.

The solvent was removed from the filtrate and the residue was washed with water and recrystallised from acetic acid and from toluene (active carbon), to give the dibromodichloro-diol (XII) (1·3 g.), m. p. 209° raised to 212° by further crystallisations from toluene and from benzene (Found: C, 30·6; H, 1·0%). Its identity with the dibromo-derivative prepared from the dichloro-diol (X) was shown by mixed m. p. and spectrograms. Out of the mother-liquor of the crystallisation from acetic acid was deposited a mustard-coloured solid (22 g.), m. p. 150—153°, which was probably impure compound (IX).[16]

The conditions of the preceding chlorination were applied to the 1,6-dibromo-diol (V) (22 g.). The initial precipitate was the dibromochloro-diol (VI) (6·7 g.), identical (m. p. and mixed m. p.) with an authentic specimen. The mother-liquor was concentrated and washed (water) to yield a substance which was chromatographed in chloroform on silica gel. The material recovered from the deep reddish-brown band was crystallised from toluene and from acetic acid to yield compound (IX) (4·0 g.), identical (m. p. and mixed m. p.) with an established sample.[16]

Reduction of the Products obtained by Chlorination of Dibromonaphthalene-2,7-diol.—The 1,6-dibromo-diol (V) (9·4 g.) was treated with sulphuryl chloride (3·5 molar proportions) as described above, and then the solvent was removed and the residue was reduced by zinc and acetic acid to give, after recrystallisation from acetic acid and from toluene (active carbon), the compound (XII) (0·33 g.), m. p. 211—212·5° (Found: C, 31·2, 30·6; H, 1·2, 0·8; Br, 40·6, 40·3; Cl, 18·0, 18·0%). Its identity was confirmed by the mixed m. p. with the dibromodichloro-diol made from the dichloro-diol (X) and by spectrograms.

Chlorine (3·3 molar proportions) was passed into crude dibromonaphthalene-2,7-diol (56 g.) in acetic acid (1·2 l.) at 45°. The product was reduced by zinc to yield a solid (19 g.), recrystallisation of which from toluene (active carbon) and from *o*-dichlorobenzene afforded the bromodichloro-diol (XI), m. p. 199° (Found: C, 38·5, 38·3; H, 2·4, 1·7%). Its identity with the product of monobromination of the dichloro-diol (X) was shown by the mixed m. p. and spectrograms. The m. p. of a mixture with 1,6-dibromo-8-chloronaphthalene-2,7-diol (VI) (m. p. 191—192°) was 191—191·5° (see comments on m. p.'s of mixtures of some chloro- and bromo-analogues in the naphthalene series [25]).

1,3,6,8-*Tetrabromonaphthalene-2,7-diol* (XXXII).—1,3,6-Tribromonaphthalene-2,7-diol (XXXI) (0·19 g.), sodium acetate trihydrate (0·19 g.), acetic acid (4·3 ml.), and bromine

[25] R. H. Thomson, *J. Org. Chem.*, 1948, **13**, 870; F. Bell and J. A. Gibson, *J.*, 1954, 4635.

(0·025 ml.) were cooled from 32° in 30 min., to yield a precipitate, which by crystallisation from toluene gave faintly pink needles (0·10 g.) of the tetrabromo-diol, m. p. 191—192° (decomp.) (Found: C, 25·7; H, 0·9; Br, 66·9. Calc. for $C_{10}H_4Br_4O_2$: C, 25·4; H, 0·8; Br, 67·2%); $\nu_{max.}$ 546w, 560, 643, 675w, 701w, 724w, 744w, 773w, 792w, 822, 839w, 862w, 899, 1020w, 1060w, 1170vs, 1200, 1215sh, 1305, 1355s, 1405s, 1445w, 1485, 1530w, 1595, 3060w, 3400s, and 3425sh cm.$^{-1}$. Its m. p. was depressed by the tribromo-diol (XXXI) (m. p. 207·5°; after 3 years this m. p. had not changed and the compound had become faintly pink). The colour of the tetrabromo-compound was pale pink after 16 months.

A similar bromination without the sodium acetate yielded only a very small precipitate. The whole mixture was therefore heated to 48° and left for 25 min. The deposit was crystallised from toluene to give the tetrabromo-diol (XXXII) (0·01 g.), identical (m. p. and mixed m. p.) with the product of the previous experiment.

1,3-*Dibromo*-2,7-*diethoxynaphthalene* (VII).—1,3-Dibromonaphthalene-2,7-diol [3] (VIII) was refluxed for 2 hr. with diethyl sulphate and potassium carbonate in acetone. Dilution with water and heating at 50° for ½ hr. afforded the theoretical yield of the *ether*, m. p. 158° [from light petroleum (b. p. 80—100°)] (Found: C, 45·0; H, 3·8; Br, 43·6, 42·5; OEt, 22·8, 25·1. $C_{14}H_{14}Br_2O_2$ requires C, 44·9; H, 3·8; Br, 42·7; 2OEt, 24·1%). The earlier product, made from crude dibromonaphthalene-2,7-diol and claimed to be the 1,6-dibromo-ether,[2] now appears to have been the 1,3-isomer.[6]

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