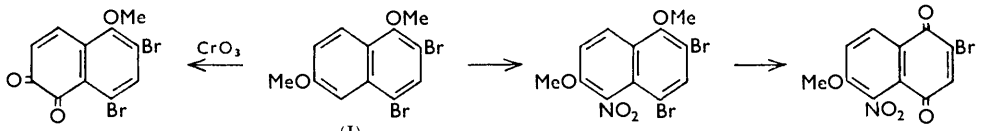
886. *Some Reactions of Dimethoxynaphthalenes.*

By F. Bell and K. R. Buck.

The nitration and halogenation of 1,5-, 1,6-, 1,7-, and 2,3-dimethoxynaphthalene are outlined. Infrared spectra of all the substitution products are recorded, and the limitations to the use of infrared spectra for orientation purposes are discussed.

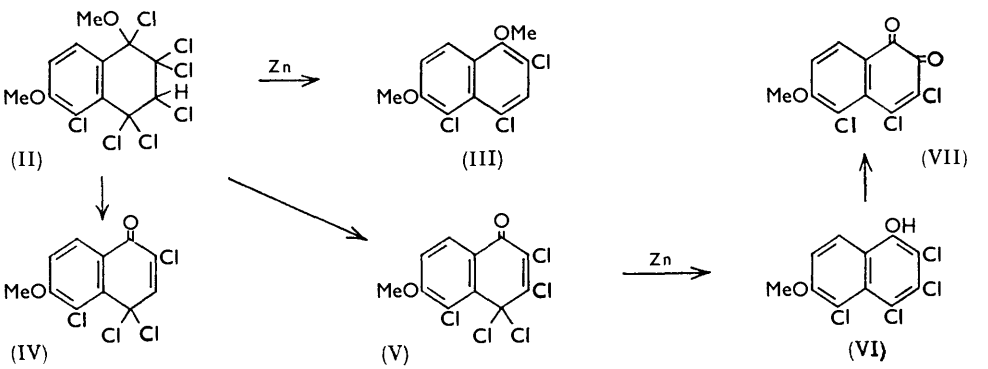
The ready production of 1,2-naphthaquinones from derivatives of 2,7-dihydroxynaphthalene [1] has prompted an examination of other dihydroxynaphthalenes, and the present paper deals with derivatives of 1,5-, 1,6-, 1,7-, and 2,3-dihydroxynaphthalene.

Bromination of 1,6-dimethoxynaphthalene gave a dibromo-derivative which, with chromic acid, gave a dibromo-1,2-naphthaquinone, and with nitric acid either a mononitro-derivative or, on prolonged treatment, a 1,4-naphthaquinone. The infrared spectrum of the dibromodimethoxynaphthalene best accorded with (I), and these reactions are interpreted accordingly.



(I)

Treatment of 1,6-dimethoxynaphthalene with sulphuryl chloride gave a heptachloro-derivative (II) which could be readily converted by zinc into a trichloro-derivative (III) but with nitric acid it gave a complex mixture from which were isolated compounds regarded as (IV) and (V). The latter was smoothly converted into a tetrachloronaphthol (VI), which could be oxidised to a trichloro-1,2-naphthaquinone (VII).



(II) (III) (VII)

(IV) (V) (VI)

Nitration of 1,6-dimethoxynaphthalene gave a mixture of two dinitro-derivatives which, with fuming nitric acid, gave trinitro-derivatives, without quinone formation. Unequivocal structures could not be assigned to these nitro-compounds from a study of their infrared spectra.

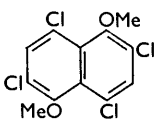
1,5-Dimethoxynaphthalene, with sulphuryl chloride, gave a tetrachloro-derivative (VIII); this, with nitric acid, gave a mixture of quinones from which were readily isolated a trichloro-1,4-naphthaquinone (IX), and a trichloro-1,2-naphthaquinone (X) as its quinoxaline derivative.

2,6-Dibromo-1,5-dihydroxynaphthalene, with nitric acid, gave a good yield of the

[1] Bell, *J.*, 1961, 5293.

nitro-1,4-naphthaquinone (XI), identical with the product of nitration of 2,6-dibromo-5-hydroxy-1,4-naphthaquinone.[2]

Carter, Race, and Rowe[3] showed that bromination of 1,5-diacetoxynaphthalene leads to 5-acetoxy-2,4-dibromo-1-naphthol. This result suggested that the bromination had involved a preliminary hydrolysis to 5-acetoxy-1-naphthol, which was then attacked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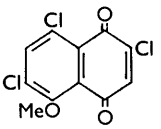
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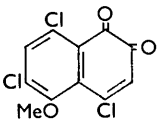
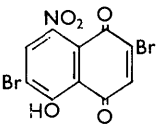

(X)

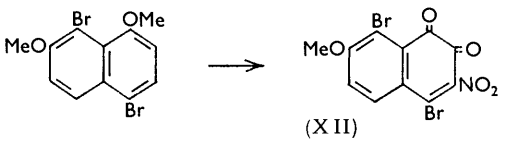

(XI)

in the 2,4-positions. When the experiment was repeated with acetic anhydride–acetic acid as solvent, the product was, surprisingly, 1,5-diacetoxy-2,4-dibromonaphthalene.

1,7-Diethoxynaphthalene gave a dibromo-derivative which was nitrated, but not oxidised, by nitric acid. It also yielded a dibromo-derivative, which was smoothly converted into a trinitro-derivative.

1,7-Dimethoxynaphthalene, on bromination, gave a mixture of two dibromo-derivatives, one of which yielded a 1,2-naphthaquinone, probably (XII), whilst the other underwent nitration.

With sulphuryl chloride, 1,7-dimethoxynaphthalene gave a trichloro-derivative, readily converted into a dichloro-1,4-naphthaquinone, regarded as (XIII), together with a 1,2-naphthaquinone, isolated as its quinoxaline derivative.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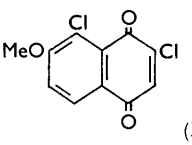
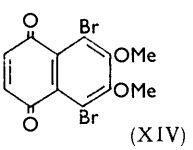

(XIII)

2,3-Dimethoxynaphthalene, with bromine (2 mol.) in chloroform, gave a dibromo-derivative, the infrared spectrum of which agreed with a 1,4-positioning of the bromine atoms, as did the oxidation to yield a dibromodimethoxy-1,4-naphthaquinone (XIV). With nitric acid, this dibromo-derivative gave a 1,2-naphthaquinone, probably (XV), and, with bromine in chloroform, an additive compound regarded as (XVI), which could be reconverted into the starting material by treatment with zinc in acetic acid. This addition compound was decomposed by solution in pyridine to give a mixture of two tribromo-derivatives, (XVII) and (XVIII), alternatively prepared by direct bromination in acetic acid. The tribromo-compound (XVII) gave, with nitric acid, a dibromonitro-1,2-naphthaquinone, probably (XIX).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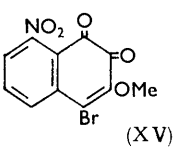
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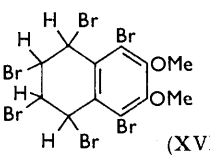
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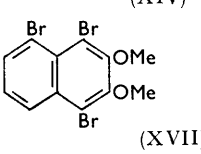
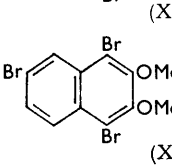
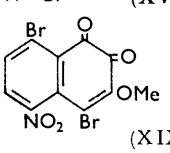

(XVII)


(XVIII)


(XIX)

Chlorination of 1,4-dibromo-2,3-dimethoxynaphthalene by sulphuryl chloride resulted in partial replacement of bromine by chlorine and consequent production of a mixture of at least three compounds.

[2] Wheeler and Ergle, *J. Amer. Chem. Soc.*, 1930, **52**, 4872.
[3] Carter, Race, and Rowe, *J.*, 1942, 236.

1,4-Dichloro-2,3-dimethoxynaphthalene was readily obtained by the interaction of 2,3-dimethoxynaphthalene with sulphuryl chloride. It could be monobrominated and dinitrated, but not oxidised to a quinone. The monobromo-derivative, with nitric acid, gave a quinone analogous to (XIX).

2,3-Dimethoxynaphthalene was smoothly mononitrated, but with more-concentrated nitric acid gave a mixture of the 1,4-dinitro-derivative and 3-methoxy-1,4-dinitro-2-naphthol; quinone formation was not observed.

Hawkins, Ward, and Whiffen [4] discussed the connection between infrared absorption frequencies and substitution patterns in the naphthalene series. Examination of the spectra of a considerable number of naphthalene derivatives has led us to the conclusion that, whilst the average values of the wave-numbers of the absorption bands in the various spectral regions agree closely with the values given by the above authors, their use as a means of determining the substitution pattern of an unknown naphthalene derivative is very limited. This is partly due to the presence of absorption bands additional to those which would be expected if naphthalene behaved as two independent substituted benzene rings, and partly due to overlapping of the absorption bands which arise from different substitution patterns. Thus, the spectrum of a given substance might fit two or three hydrogen patterns, or even none at all. However, we have found that 1,2,3,4, 1,2,4, and 2,3 hydrogen patterns can generally be picked out with a fair measure of success, whereas 1 or 2, 1,2, 1,3, and 1,4 hydrogen patterns are almost valueless for diagnostic purposes.

Experimental

Infrared spectra were taken for potassium bromide discs. Compounds were recrystallised from acetic acid unless otherwise stated. Process (A) indicates the addition of the compound (1 g.) to a mixture of fuming nitric acid (5 c.c.) and acetic acid (5 c.c.); (C) means that the product crystallised from the reaction mixture, and (P) that it was obtained by precipitation with water. An asterisk indicates a preferred but not rigidly proved structure.

2,4-*Dibromo*-1,6-*dimethoxynaphthalene* (I).—Bromine (3·4 g.) in chloroform (3 c.c.) was added drop-wise to 1,6-dimethoxynaphthalene (2 g.) in chloroform (20 c.c.). After the vigorous evolution of hydrogen bromide, the solvent was removed, and the residue yielded the *product* as needles (3 g.), m. p. 97° (from ethanol) (Found: C, 41·2; H, 3·0. $C_{12}H_{10}Br_2O_2$ requires C, 41·7; H, 2·9%); $\nu_{max.}$ (diagnostic bands) 719s, 764s, 826vs, 839vs, 890s, 952vs, 985s, 1032vs, 1078s, 1160s, 1214s, 1240 cm.$^{-1}$, (other strong bands) 1344, 1410, 1452, 1505, 1590, 1625 cm.$^{-1}$. Chromic acid (3 g.) in water (3 c.c.) was added to this compound (3 g.) in acetic acid (20 c.c.) at 60°. After the vigorous reaction, the mixture was poured into water and the product, crystallised from acetic acid and then benzene, gave 6,8-*dibromo*-5-*methoxy*-1,2-*naphthaquinone* as red needles, m. p. 222° (decomp.) (Found: C, 39·2; H, 1·9. $C_{11}H_6Br_2O_3$ requires C, 38·2; H, 1·7%), $\nu_{max.}$ 730s, 790, 810s, 846s, 879s, 970vs, 1048s, 1125, 1180vs, 1240vs, 1290, 1355s, 1410, 1450, 1530s, 1670vs cm.$^{-1}$. It gave a deep violet colour with sulphuric acid. With *o*-phenylenediamine in acetic acid *the quinoxaline*, yellow needles, m. p. 208°, was formed (Found: C, 48·9; H, 2·5. $C_{17}H_{10}Br_2N_2O$ requires C, 48·8; H, 2·4%).

Interaction of 2,4-*Dibromo*-1,6-*dimethoxynaphthalene with Nitric Acid.*—Fuming nitric acid (2 c.c.) in acetic acid (6 c.c.) was added to a warm solution of the compound (2 g.) in acetic acid (20 c.c.). On cooling, the solution deposited crystals (0·6 g.), m. p. 110—135°, best purified by chromatography from acetone on alumina. The first fraction gave the *mononitro-derivative* as pale yellow needles, m. p. 126° (Found: C, 36·9; H, 2·4. $C_{12}H_9Br_2NO_4$ requires C, 36·8; H, 2·3%), $\nu_{max.}$ 720, 745, 780, 798, 829vs, 872s, 910s, 952vs, 1005vs, 1085vs, 1120s, 1230, 1280vs, 1340vs, 1375s, 1455, 1500s, 1540vs, 1580, 1620s cm.$^{-1}$. The main filtrate was kept at 70°, and bright yellow crystals slowly separated, which gave 2-*bromo*-6-*methoxy*-5-*nitro*-1,4-*naphthaquinone* * as prisms, m. p. 286—288° (decomp.) (Found: C, 42·5; H, 2·0. $C_{11}H_6BrNO_5$ requires C, 42·3; H, 1·9%), which did not give a colour with sulphuric acid or a precipitate with *o*-phenylenediamine; $\nu_{max.}$ 742, 794s, 805, 819, 855s, 900s, 928, 1040vs, 1085, 1235, 1300vs,

[4] Hawkins, Ward, and Whiffen, *Spectrochim. Acta*, 1958, **10**, 105.

1325, 1375, 1490, 1560s, 1590vs, 1670vs, 1685vs cm.$^{-1}$. This quinone was the only product from the dibromo-compound in process (A).

Chlorination of 1,6-*Dimethoxynaphthalene.*—Excess of sulphuryl chloride was added to the compound and after the brisk reaction the excess was evaporated. The residual oil was dissolved in hot methanol and allowed to cool; the crystals yielded 1,2,2,3,4,4,5-*heptachloro*-1,6-*dimethoxytetralin* (II) as needles, m. p. 92—94° (from methanol) (Found: C, 33·6; H, 2·0. $C_{12}H_9Cl_7O_2$ requires C, 33·2; H, 2·1%), $\nu_{max.}$ 709, 727, 782s, 819, 825, 918vs, 938s, 968s, 1060, 1162s, 1195s, 1265, 1375, 1418, 1455s, 1550 cm.$^{-1}$. It was unchanged (Found: C, 33·6; H, 2·3%) by solution in hot pyridine. The structure was confirmed by treating the compound in boiling acetic acid with zinc dust; 2,4,5-*trichloro*-1,6-*dimethoxynaphthalene* (III) was obtained as fine needles, m. p. 98° (from ethanol) (Found: C, 49·6; H, 3·0. $C_{12}H_9Cl_3O_2$ requires C, 49·4; H, 3·1%), $\nu_{max.}$ 711, 770, 784, 814, 818, 864, 913, 958s, 999vs, 1075s, 1105s, 1225, 1270vs, 1285s, 1315s, 1370vs, 1440, 1460, 1498, 1590, 1610 cm.$^{-1}$.

Interaction of Heptachloro-1,6-*dimethoxytetralin with Nitric Acid.*—Process (A). No visible reaction occurred but the compound very slowly dissolved. The filtered solution was poured into water, and the yellow precipitate freed from naphthols by warm aqueous sodium hydroxide and then separated by fractional crystallisation from ethanol into 2,4,4,5-*tetrachloro*-6-*methoxy*-1-*dialone* (IV), needles, m. p. 128° (Found: C, 42·2; H, 2·5. $C_{11}H_6Cl_4O_2$ requires C, 42·3; H, 1·9%), $\nu_{max.}$ 692, 758, 768, 806, 829, 867, 882, 920, 952, 1005s, 1025, 1138s, 1182vs, 1200vs, 1260s, 1470s, 1490, 1770 cm.$^{-1}$, and 2,3,4,4,5-*pentachloro*-6-*methoxy*-1-*dialone* (V), pale yellow prisms, m. p. 135—137° (Found: C, 38·2; H, 1·6. $C_{11}H_5Cl_5O_2$ requires C, 38·1; H, 1·4%), $\nu_{max.}$ 679, 703s, 735, 768s, 822s, 845, 882s, 923, 963vs, 991, 1068s, 1155, 1215vs, 1258s, 1322s, 1387, 1425, 1455, 1555, 1710 cm.$^{-1}$. A solution of the latter in boiling acetic acid gave, with zinc dust, 2,3,4,5-*tetrachloro*-5-*methoxy*-1-*naphthol* (VI), which formed needles, m. p. 160° (from ethanol) (Found: C, 41·9; H, 2·1. $C_{11}H_6Cl_4O_2$ requires C, 42·3; H, 1·9%), $\nu_{max.}$ 673, 769, 804, 873, 894, 952, 973vs, 1118s, 1185, 1242, 1275, 1325vs, 1392, 1438, 1585vs, 3500ms cm.$^{-1}$.

Interaction of 2,3,4,5-*Tetrachloro*-6-*methoxy*-1-*naphthol with Nitric Acid.*—Processes (A) and (P) gave 3,4,5-*trichloro*-6-*methoxy*-1,2-*naphthaquinone* (VII) as vermilion needles, m. p. 172—174° (Found: C, 45·4; H, 1·7. $C_{11}H_5Cl_3O_3$ requires C, 45·3; H, 1·7%), $\nu_{max.}$ 694, 752, 772, 859s, 877ms, 905, 924ms, 959s, 988, 1048, 1168, 1208vs, 1255s, 1287, 1335s, 1385, 1425ms, 1465ms, 1548ms, 1700vs cm.$^{-1}$; *the quinoxaline* formed pale yellow needles, m. p. 218° (Found: C, 56·4; H, 2·6. $C_{17}H_9Cl_3N_2O$ requires C, 56·1; H, 2·5%), and gave an indigo colour with sulphuric acid.

Nitration of 1,6-*Dimethoxynaphthalene.*—(*a*) Fuming nitric acid (1 c.c.) in acetic acid (2 c.c.) was added to a warm solution of the compound (1 g.) in acetic acid (10 c.c.). On cooling, the mixture slowly deposited needles, which gave the *dinitro-derivative*, m. p. 203—204° (Found: C, 51·7; H, 3·5. $C_{12}H_{10}N_2O_6$ requires C, 51·8; H, 3·6%), $\nu_{max.}$ 748, 780s, 790, 816, 824s, 838, 880, 914ms, 1028vs, 1092s, 1120s, 1190, 1210, 1260s, 1270ms, 1325vs, 1418, 1450, 1540vs, 1575, 1640 cm.$^{-1}$. More of the same compound, but rather red in colour, was obtained by keeping the main filtrate at 70° for some time. Finally, the filtrate was reheated and gradually diluted with about an equal volume of water. The material which separated on cooling gave the 2,4-*dinitro-derivative* as lustrous, pale yellow plates, m. p. 138° (from ethanol–ethyl acetate) (Found: C, 51·9; H, 3·9%); $\nu_{max.}$ (diagnostic bands) 734, 788, 818s, 845s, 861s, 898, 916, 930w, 962, 1008s, 1023s, 1092ms, 1150, 1186, 1225, 1245s, 1262s, (other strong bands) 1320, 1350, 1420, 1460, 1510, 1590, 1615 cm.$^{-1}$.

(*b*) The dinitro-derivative in processes (A) and (P) gave a *trinitro-compound* as rosettes of needles m. p. 158—160° (from ethyl acetate) (Found: C, 45·1; H, 2·8. $C_{12}H_9N_3O_8$ requires C, 44·5; H, 2·8%), $\nu_{max.}$ 732, 800s, 812s, 840s, 868, 902, 960, 970, 1005ms, 1086s, 1125, 1190, 1235, 1275vs, 1315, 1340vs, 1370, 1430, 1460ms, 1540vs, 1580s, 1620 cm.$^{-1}$.

(*c*) When the 2,4-dinitro-compound was submitted to processes (A) and (C) it gave a *trinitro-compound*, m. p. 164—166° (Found: C, 45·1; H, 2·7%), which formed small prisms from ethyl acetate; $\nu_{max.}$ 714, 728, 742, 760, 800s, 815s, 836s, 873s, 905s, 960s, 975, 1008s, 1090vs, 1128, 1165, 1185, 1280vs, 1340vs, 1430, 1460, 1500, 1550vs, 1590s, 1640s cm.$^{-1}$.

Bromination of 1,5-*Dimethoxynaphthalene.*—Bromine (3·2 g.) in chloroform (3 c.c.) was added to a warm solution of the compound (1·88 g.) in chloroform (20 c.c.). After the brisk reaction the solution was evaporated, and the dark sticky residue yielded a mixture of dibromo-derivatives, m. p. *ca.* 145° (from acetic acid) (Found: C, 41·9; H, 2·8. Calc. for $C_{12}H_{10}Br_2O_2$ C, 41·6; H, 2·9%). Further recrystallisation from carbon tetrachloride and then ethanol

gave the 2,6-dibromo-derivative as needles, m. p. 158—159°, $\nu_{max.}$ 718, 815, 838s, 900s, 1030vs, 1132, 1170w, 1198, 1230, 1300, 1380vs, 1450, 1580s cm.$^{-1}$. Bergmann [5] isolated this compound in 20% yield by bromination in benzene; bromination in acetic acid gives the 4,8-dibromo-compound, m. p. 187°.[3]

Chlorination of 1,5-*Dimethoxynaphthalene.*—The compound was covered with an excess of sulphuryl chloride and after reaction had ceased the excess was removed. The residual solid gave the *tetrachloro-derivative* * (VIII) as needles, m. p. 201° (Found: C, 44·3; H, 2·4. $C_{12}H_8Cl_4O_2$ requires C, 44·2; H, 2·5%), $\nu_{max.}$ 707, 758, 848, 869, 920s, 1032vs, 1225, 1265, 1348vs, 1575s cm.$^{-1}$.

Interaction of 2,4,6,8-*Tetrachloro*-1,5-*dimethoxynaphthalene with Nitric Acid.*—Process (A) gave pale yellow crystals which dissolved in boiling acetic acid with gas evolution; on cooling there separated yellow needles of 2,6,8-*trichloro*-5-*methoxy*-1,4-*naphthaquinone* (IX), m. p. 141° (Found: C, 45·3; H, 1·7. $C_{11}H_5Cl_3O_3$ requires C, 45·3; H, 1·7%), readily sublimable and giving no colour with sulphuric acid; $\nu_{max.}$ 776, 844, 869, 889, 934vs, 1015s, 1112s, 1212vs, 1225, 1282s, 1318, 1365s, 1412s, 1460s, 1540, 1620s, 1660vs, 1680vs. cm.$^{-1}$. The mother-liquor contained a small amount of a trichloro-5-methoxy-1,2-naphthaquinone (X) which gave a purple colour with sulphuric acid, and with *o*-phenylenediamine *a quinoxaline* which formed yellow needles, m. p. 216—218° (Found: C, 55·8; H, 2·1. $C_{17}H_9Cl_3N_2O$ requires C, 56·1; H, 2·5%), and gave an indigo colour with sulphuric acid.

Bromination of 1,5-*Diacetoxynaphthalene.*—(*a*) Bromination by the method of Carter, Race, and Rowe [3] gave 5-acetoxy-2,4-dibromo-1-naphthol, m. p. 172°; it was acetylated in pyridine to 1,5-diacetoxy-2,4-dibromonaphthalene, m. p. 131°.

(*b*) Bromine (3·2 g.) in acetic acid was added to a solution of 1,5-diacetoxynaphthalene (2·4 g.) in a mixture of acetic acid (10 c.c.) and acetic anhydride (5 c.c.). After some hours the mixture was poured into water and the plastic product separated by decantation. It was solidified by trituration with ethanol and the product (3·2 g.) purified by repeated recrystallisation from benzene to yield 1,5-diacetoxy-2,4-dibromonaphthalene (above).

Interaction of 2,6-*dibromo*-1,5-*dihydroxynaphthalene with Nitric Acid.*—Processes (A) and (C) gave 2,6-*dibromo*-5-*hydroxy*-8-*nitro*-1,4-*naphthaquinone* * as orange prisms, m. p. 220° (Found: C, 32·1; H, 1·1. $C_{10}H_3Br_2NO_5$ requires C, 31·9; H, 0·8%), identical with the product obtained by nitration of 2,6-dibromo-5-hydroxy-1,4-naphthaquinone; $\nu_{max.}$ 683, 704, 749, 833s, 912ms, 973, 1102, 1125, 1215s, 1225s, 1342, 1375, 1420s, 1550s, 1590, 1645ms, 1685ms cm.$^{-1}$.

The Nitration of 1,7-*Diethoxynaphthalene.*—(*a*) Fuming nitric aid (1 c.c.) in acetic acid (1·5 c.c.) was added to a slightly warm solution of the compound (1 g.) in acetic acid (10 c.c.). Heat was evolved and the whole set to a yellow crystalline mass, which was filtered and washed with acetic acid. The product (1·2 g.), m. p. 180—183°, gave the dinitro-derivative as prisms, m. p. 185° (Found: C, 54·7; H, 4·3. $C_{14}H_{14}N_2O_6$ requires C, 54·9; H, 4·6%), $\nu_{max.}$ 733, 746s, 788w, 812vs, 842, 861s, 888s, 1055vs, 1112s, 1130, 1168, 1275vs, 1330vs, 1380, 1395, 1410, 1460s, 1480s, 1520vs, 1550vs, 1570s, 1610s cm.$^{-1}$.

(*b*) By processes (A) and (P) the dinitro-compound was converted into the *trinitro-derivative*, which formed golden needles, m. p. 129—130° (Found: C, 48·5; H, 3·7. $C_{14}H_{13}N_3O_8$ requires C, 47·9; H, 3·7%), $\nu_{max.}$ 796, 823vs, 840s, 877s, 896, 910w, 998, 1045vs, 1084, 1108, 1130, 1200, 1235s, 1284vs, 1340s, 1365s, 1415, 1445, 1475, 1510, 1550vs, 1580, 1610s cm.$^{-1}$.

Bromination of 1,7-*Diethoxynaphthalene.*—Bromine (2·9 g.) in chloroform (5 c.c.) was added to the compound (2 g.) in chloroform (10 c.c.). The solvent was then removed and the dark green product yielded the *dibromo-derivative* as needles, m. p. 99° (Found: C, 45·2; H, 4·2. $C_{14}H_{14}Br_2O_2$ requires C, 44·9; H, 3·7%), $\nu_{max.}$ 749, 820, 856, 870, 900, 935, 1020, 1046s, 1110, 1118, 1225vs, 1260vs, 1345, 1385, 1430, 1495, 1570, 1620s cm.$^{-1}$. Fuming nitric acid (1 c.c.) in acetic acid (1 c.c.) was added to a hot solution of this dibromo-compound (1 g.) in acetic acid (10 c.c.). On cooling, crystals separated which gave the *dibromonitro-derivative* as needles, m. p. 99° (large depression on admixture with the un-nitrated compound) (Found: C, 39·3; H, 3·1. $C_{14}H_{13}Br_2NO_4$ requires C, 40·1; H, 3·1%), $\nu_{max.}$ 750, 785, 808s, 855, 878s, 1028s, 1055, 1120, 1165, 1210s, 1265vs, 1290s, 1335s, 1360, 1435, 1500, 1545vs, 1570, 1620 cm.$^{-1}$.

Nitration of 1,7-*Dimethoxynaphthalene.*—Fuming nitric acid (4 c.c.) in acetic acid (4 c.c.) was added to the compound (4 g.; b. p. 140°/10 mm.) in acetic acid (40 c.c.). Crystals began to appear before the addition was complete, and after ½ hr. they were filtered off (4·7 g.) and

[5] Bergmann, *J.*, 1948, 1283.

washed with acetic acid. Recrystallisation gave the *dinitro-derivative* as prisms, m. p. 207—209° (Found: C, 52·0; H, 3·3. $C_{12}H_{10}N_2O_6$ requires C, 51·8; H, 3·6%), $\nu_{max.}$ 756, 850, 926, 993, 1010, 1020, 1036, 1250, 1325s, 1365, 1400s, 1460, 1530, 1680s cm.$^{-1}$. Chromic acid oxidation of this nitro-compound gave no isolable product. Processes (A) and (C) gave material, m. p. *ca.* 170°, best purified by solution in acetic acid, which left undissolved a small amount of an orange-red material (gradual decomposition above 200°) which had the infrared characteristics of a hydroxy-quinone. The *trinitro-compound* formed needles, m. p. 177—179° (Found: C, 44·5; H, 2·6. $C_{12}H_9N_3O_8$ requires C, 44·5; H, 2·8%), $\nu_{max.}$ 722, 757, 800, 830s, 850ms 895vs, 965, 1052vs, 1094s, 1135, 1190, 1250s, 1285vs, 1330s, 1370s, 1415s, 1470, 1550vs, 1575, 1610s cm.$^{-1}$.

Bromination of 1,7-*Dimethoxynaphthalene.*—(*a*) Bromine (6·8 g.) in chloroform was added to the compound (4 g.) in chloroform (20 c.c.) and the solvent removed. The residual oil was dissolved in acetic acid; the solution slowly deposited crystals during several days. The first crop (1·1 g., m. p. *ca.* 120°) gave the 4,8-*dibromo-derivative* as needles, m. p. 124—126° (Found: C, 41·9; H, 2·7. $C_{12}H_{10}Br_2O_2$ requires C, 41·6; H, 2·9%), $\nu_{max.}$ 718w, 800, 820vs, 855s, 920, 932, 992, 1032s, 1092s, 1130, 1160, 1182, 1225s, 1240vs, 1275s, 1325vs, 1380, 1395, 1420, 1440, 1470s, 1505s, 1590s, 1625s cm.$^{-1}$. The latter crops, of lower m. p., were boiled with light petroleum and filtered from the dibromo-compound. The more soluble material gave the 2(?),4(?)-*dibromo-compound* in lustrous needles, m. p. 65—67° (from methanol) (Found: C, 41·7; H, 2·7%), $\nu_{max.}$ 719s, 732s, 765, 820s, 845s, 855, 862, 914s, 950, 988s, 1040s, 1065, 1140, 1180, 1225vs, 1265vs, 1350s, 1420s, 1435s, 1450, 1470, 1500s, 1580s, 1630s cm.$^{-1}$. Oxidation of both dibromo-compounds in acetic acid by chromic acid led only to resinous material.

(*b*) The same procedure as in (*a*), but using 3 mol. of bromine, gave a far from uniform product from which was isolated by fractional crystallisation from ethyl acetate a *tetrabromo-derivative* in needles, m. p. 174° (Found: C, 29·2; H, 1·7. $C_{12}H_8Br_4O_2$ requires C, 28·6; H, 1·6%), $\nu_{max.}$ 702, 758, 773, 800vs, 855w, 923, 942, 990vs, 1060vs, 1100, 1160s, 1255vs, 1310s, 1335, 1385, 1440, 1475, 1530, 1600 cm.$^{-1}$. This compound did not react smoothly with nitric acid and no pure compound was isolated.

Interaction of 4,8-*Dibromo*-1,7-*dimethoxynaphthalene with Nitric Acid.*—Processes (A) and (C) gave red crystals, m. p. *ca.* 220°, which, after two recrystallisations from *o*-dichlorobenzene, gave 4,8-*dibromo*-7-*methoxy*-3-*nitro*-1,2-*naphthaquinone* * (XII), m. p. 318° (decomp.) (Found: C, 34·0; H, 1·6. $C_{11}H_5Br_2NO_5$ requires C, 33·8; H, 1·3%), $\nu_{max.}$ 694s, 754, 804, 840, 862, 990s, 1018w, 1115, 1180w, 1230, 1255, 1300vs, 1380, 1430w, 1480, 1550vs, 1600, 1690vs, 1710w cm.$^{-1}$. This compound gave no colour with sulphuric acid; with *o*-phenylenediamine it gave *the quinoxaline* as yellow needles, m. p. 264° (Found: C, 44·4; H, 1·9. $C_{17}H_9Br_2N_3O_3$ requires C, 44·0; H, 1·9%), which gave a red-brown colour with sulphuric acid. The *o*-dichlorobenzene mother-liquors contained another 1,2-naphthaquinone, since, with *o*-phenylenediamine, there was obtained a brownish-yellow precipitate, m. p. *ca.* 300°, almost insoluble in boiling acetic acid; it gave a crimson colour with sulphuric acid.

Interaction of 2,4(?)-*Dibromo*-1,7-*dimethoxynaphthalene with Nitric Acid.*—Processes (A) and (P) gave a *dinitro-derivative*, m. p. 186°, as pale yellow needles which gave no colour with sulphuric acid (Found: C, 33·0; H, 1·9; N, 6·1; OMe, 14·4. $C_{12}H_8Br_2N_2O_6$ requires C, 33·0; H, 1·8; N, 6·4; 2OMe, 14·2%), $\nu_{max.}$ 686, 740, 770, 790, 815s, 850s, 915, 955, 965s, 1045, 1070s, 1130, 1175, 1280vs, 1340s, 1380s, 1420, 1460s, 1500s, 1550vs, 1620 cm.$^{-1}$. The mother-liquor contained a trace of a compound, as yellow prisms, m. p. 236°, which had the spectral characteristics of a quinone, and which gave a cherry-red colour with sulphuric acid.

Chlorination of 1,7-*Dimethoxynaphthalene.*—Excess of sulphuryl chloride was added to the compound, and after the brisk reaction the excess was evaporated. The semi-solid residue, crystallised from methanol and then acetic acid, yielded the 2,4,8-*trichloro-derivative* as needles, m. p. 108—110° (Found: C, 49·6; H, 2·9. $C_{12}H_9Cl_3O_2$ requires C, 49·4; H, 3·1%), $\nu_{max.}$ 711, 752, 760, 795, 805, 855, 930, 965, 1020, 1070, 1108, 1165, 1270vs, 1320, 1340w, 1400, 1450, 1500, 1550, 1580, 1610 cm.$^{-1}$.

Interaction of 2,4,8-*Trichloro*-1,7-*dimethoxynaphthalene with Nitric Acid.*—Processes (A) and (P) gave 2,8-*dichloro*-7-*methoxy*-1,4-*naphthaquinone* * (XIII) as orange needles, m. p. 187—189° (Found: C, 51·5; H, 2·2. $C_{11}H_6Cl_2O_3$ requires C, 51·4; H, 2·3%), $\nu_{max.}$ 677s, 697, 723s, 845s, 884, 927vs, 1022, 1098s, 1125, 1205, 1278vs, 1335s, 1438, 1472, 1575s, 1585s, 1610, 1660s, 1690s cm.$^{-1}$; it gave a purple colour with sulphuric acid. The acetic acid mother-liquors contained a mixture of 1,2-quinones which gave with *o*-phenylenediamine a product, m. p. *ca.* 200°, from

which, by repeated recrystallisation from acetic acid, there could be isolated, almost pure, *the quinoxaline*, m. p. 243° (Found: C, 55·4; H, 2·3. $C_{17}H_9Cl_2N_3O_3$ requires C, 54·5; H, 2·4%), from a 5,7-dichloro-8-methoxynitro-1,2-naphthaquinone.

Interaction of 2,3-*Dimethoxynaphthalene with Bromine.*—(*a*) Bromine (6·9 g.) in chloroform was added drop-wise to a solution of the compound (4 g.) in chloroform (20 c.c.). After the brisk evolution of hydrogen bromide the solvent was removed; the residue gave the 1,4-*dibromo-derivative* in needles, m. p. 76—78° (from ethanol) (Found: C, 41·5; H, 2·8. $C_{12}H_{10}Br_2O_2$ requires C, 41·6; H, 2·9%), $\nu_{max.}$ 750vs, 920s, 990s, 1020s, 1043, 1120, 1150w, 1165w, 1240s, 1320, 1360, 1395vs, 1460s, 1550w, 1580w cm.$^{-1}$. The same compound was obtained in poorer yield by bromination in acetic acid.

(*b*) Bromine (6·4 g.) in chloroform was added to the compound (1·88 g.) in chloroform (12 c.c.). When evolution of hydrogen bromide had ceased the mixture was diluted with light petroleum and filtered from a precipitate (1·6 g.); the solvent was then removed and the sticky residue recrystallised to yield needles (1·8 g.), m. p. 120—123°, of the 1,4,5-*tribromo-derivative* (XVII) (Found: C, 33·9; H, 2·4. $C_{12}H_9Br_3O_2$ requires C, 33·9; H, 2·1%), $\nu_{max.}$ 672, 762, 769, 802s, 867, 932vs, 988vs, 1025s, 1078, 1125, 1225s, 1295, 1332, 1355s, 1395vs, 1455s, 1680 cm.$^{-1}$. The precipitate, on recrystallisation, gave 1,4,5,6,7,8-*hexabromo*-2,3-*dimethoxy*-5,6,7,8-*tetralin* (XVI) as needles, m. p. 170° (decomp.) (Found: C, 22·1; H, 1·5. $C_{12}H_{10}Br_6O_2$ requires C, 21·6; H, 1·5%), $\nu_{max.}$ 702w, 760, 778w, 800, 875s, 970s, 1020s, 1100s, 1230, 1300s, 1396s, 1455s, 1560w cm.$^{-1}$. This decomposed in pyridine to give mainly 1,4,6-*tribromo*-2,3-*dimethoxynaphthalene* (XVIII), which formed needles, m. p. 192° (Found: C, 34·0; H, 2·2%), $\nu_{max.}$ 734, 754w, 834, 858s, 874w, 948, 1005, 1035, 1135, 1250s, 1285, 1340, 1410, 1480s, 1580, 1610w cm.$^{-1}$. On addition of zinc to a suspension of the hexabromo-compound in boiling acetic acid there was obtained as the main product 1,4-dibromo-2,3-dimethoxynaphthalene.

(*c*) Bromine (7 g.) in acetic acid (3 c.c.) was added to a warm solution of the compound (4 g.) in acetic acid (20 c.c.). After a short time the mixture was poured into water and the sticky precipitate separated by decantation. Repeated recrystallisation from ethanol gave the 1,4,5-tribromo-derivative; the accompanying 1,4,6-tribromo-derivative was best purified by taking advantage of its much lower solubility in light petroleum. The same mixture of tribromo-compounds was obtained even when a much higher proportion of bromine was used in this experiment.

Oxidation of 1,4-*Dibromo*-2,3-*dimethoxynaphthalene.*—Chromium trioxide (2 g.) in the minimum of water was added to the compound (2·5 g.) in acetic acid (20 c.c.) at 50°. After ½ hr. the mixture was poured into water, and the precipitate gave 5,8-*dibromo*-6,7-*dimethoxy*-1,4-*naphthaquinone* (XIV) as needles, m. p. 160° (from methanol) (Found: C, 37·8; H, 2·3. $C_{12}H_8Br_2O_4$ requires C, 38·3; H, 2·1%), $\nu_{max.}$ 848, 932, 1000s, 1030s, 1210, 1248, 1320vs, 1392s, 1445, 1510, 1530, 1670vs cm.$^{-1}$; it gave a chocolate colour with sulphuric acid. This was a very variable reaction, with free bromine as a product; at times the yield of quinone was negligible and on one occasion a small amount of 1,4,5-tribromo-2,3-dimethoxynaphthalene was isolated.

Interaction of 1,4-*Dibromo*-2,3-*dimethoxynaphthalene with Nitric Acid.*—Processes (A) and (P) gave 4-*bromo*-3-*methoxy*-8-*nitro*-1,2-*naphthaquinone* * as lustrous copper-coloured scales, m. p. 196° (Found: C, 42·3; H, 1·8. $C_{11}H_6BrNO_5$ requires C, 42·3; H, 1·9%), $\nu_{max.}$ 702, 733, 800, 809, 829, 843, 922, 954, 1078s, 1195, 1265, 1285, 1325vs, 1355s, 1435, 1445, 1535s, 1590, 1680vs, 1710 cm.$^{-1}$. This gave *a quinoxaline* as yellow needles, m. p. 222° (Found: C, 53·1; H, 2·6. $C_{17}H_{10}BrN_3O_3$ requires C, 53·1; H, 2·6%).

Chlorination of 1,4-*Dibromo*-2,3-*dimethoxynaphthalene.*—The compound was heated on a steam-bath with excess of sulphuryl chloride; some bromine was evolved. The excess of sulphuryl chloride was evaporated and the residual oil dissolved in ethanol. The sticky product after three further recrystallisations from ethanol formed long needles, m. p. 82—84° (Found: C, 39·0; H, 2·65%). Gas chromatography showed that this apparently uniform product was a mixture of four compounds, formed by partial replacement of bromine by chlorine. The mother-liquor contained a considerable amount of the starting material.

1,4-*Dichloro*-2,3-*dimethoxynaphthalene.*—This was readily prepared in almost quantitative yield by the interaction of 2,3-dimethoxynaphthalene with sulphuryl chloride, and formed plates, m. p. 71° (from ethanol) (Found: C, 56·2; H, 3·9. $C_{12}H_{10}Cl_2O_2$ requires C, 56·1; H, 3·9%), $\nu_{max.}$ 750s, 774, 928, 1000s, 1023s, 1045, 1118, 1245s, 1330, 1345w, 1365, 1398s, 1460s, 1590 cm.$^{-1}$. Addition of chromic acid to its solution in acetic acid resulted largely in complete

destruction. The residue of essentially unchanged material showed infrared bands corresponding to a quinone impurity.

5-Bromo-1,4-dichloro-2,3-dimethoxynaphthalene.—Bromine (3 g.) in acetic acid (2 c.c.) was added to a solution of the dichloro-compound (2·4 g.) in warm acetic acid (20 c.c.) and the mixture left overnight. The crop (1·2 g.) was recrystallised from ethanol to yield the *product* * as needles, m. p. 99—100° (Found: C, 43·2; H, 2·7. $C_{12}H_9BrCl_2O_2$ requires C, 42·8; H, 2·7%), $\nu_{max.}$ 682, 724w, 768w, 794w, 804vs, 880, 924, 940s, 998vs, 1032s, 1080s, 1125, 1225, 1300, 1365, 1395s, 1460s, 1580 cm.$^{-1}$. The acetic acid filtrate, on precipitation, gave sticky material from which was isolated the same bromo-derivative (0·8 g.). Submitted to processes (A) and (P), this compound gave *bromo-4-chloro-3-methoxy-nitro-1,2-naphthaquinone* as crimson needles, m. p. 242° (Found: C, 38·2; H, 1·6. $C_{11}H_5BrClNO_5$ requires C, 38·1; H, 1·4%), $\nu_{max.}$ 708, 724w, 742w, 838s, 932, 995w, 1055, 1085s, 1185w, 1215, 1265, 1280, 1330vs, 1370, 1452, 1560vs, 1590s, 1690s cm.$^{-1}$. This compound gave a red-brown colour with sulphuric acid, and a yellow *quinoxaline*, m. p. 208°, which gave an orange colour with sulphuric acid (Found: C, 48·5; H, 2·3. $C_{17}H_9BrClN_3O$ requires C, 48·7; H, 2·2%).

Interaction of 1,4-Dichloro-2,3-dimethoxynaphthalene with Nitric Acid.—Processes (A) and (P) gave the *5,7-dinitro-derivative*,* m. p. 174° (Found: C, 41·5; H, 2·5. $C_{12}H_8Cl_2N_2O_6$ requires C, 41·5; H, 2·3%), $\nu_{max.}$ 700, 738, 758w, 798, 840, 860, 910, 964, 1012, 1030, 1060, 1108w, 1145w, 1250, 1300w, 1340s, 1395s, 1455, 1540vs cm.$^{-1}$.

Interaction of 1,4,5-Tribromo-2,3-dimethoxynaphthalene with Nitric Acid.—Processes (A) and (P) gave a *4,8-dibromo-3-methoxy-nitro-1,2-naphthaquinone* * (XIX) as dark red plates, m. p. 245° (Found: C, 34·0; H, 1·6. $C_{11}H_5Br_2NO_5$ requires C, 33·8; H, 1·3%), $\nu_{max.}$ 704, 718, 734w, 822, 832, 842, 933, 1045, 1082s, 1145, 1185, 1215, 1260s, 1280s, 1320vs, 1370, 1400w, 1435, 1450, 1560vs, 1590, 1690vs cm.$^{-1}$. This gave *a quinoxaline* which formed yellow needles, m. p. 216° (Found: C, 44·3; H, 2·1. $C_{17}H_9Br_2N_3O_3$ requires C, 44·0; H, 1·9).

The Nitration of 2,3-Dimethoxynaphthalene.—(*a*) Fuming nitric acid (2 c.c.) in acetic acid (2 c.c.) was added drop-wise to a solution of the compound (2 g.) in acetic acid (14 c.c.) at 60°. No crystallisation occurred on cooling, so the mixture was poured into water, and the resultant red oil, crystallised from ethanol and then ethyl acetate, gave the *1-nitro-derivative* as plates, m. p. 152—154° (Found: C, 61·7; H, 4·7. $C_{12}H_{11}NO_4$ requires C, 61·8; H, 4·7%), $\nu_{max.}$ 742s, 774, 813, 838, 848, 868s, 890, 1018s, 1040, 1138s, 1185, 1204, 1238, 1270vs, 1318vs, 1360, 1440, 1490s, 1520vs, 1605, 1625 cm.$^{-1}$. The mother-liquor contained a number of compounds, none of which was isolated pure.

(*b*) As in (*a*) but using 6 c.c. of fuming nitric acid. On cooling there separated a yellow precipitate which, recrystallised from ethanol and then ethyl acetate, gave *3-methoxy-1,4-dinitro-2-naphthol* as needles, m. p. 214—216° (decomp.) (Found: C, 50·6; H, 3·2. $C_{11}H_8N_2O_6$ requires C, 50·0; H, 3·0%), $\nu_{max.}$ 738, 789, 824w, 842w, 858s, 900s, 1000s, 1058, 1128w, 1165s, 1200, 1265, 1290, 1345vs, 1510vs, 1555s, 1620 cm.$^{-1}$.

(*c*) Fuming nitric acid (2 c.c.) was added drop-wise to a cooled solution of the compound (2 g.) in acetic anhydride (10 c.c.). After standing overnight there had separated material (1·2 g.), m. p. 140—180°, from which most of the impurities could be removed by acetone. The residue, on recrystallisation, gave *2,3-dimethoxy-1,4-dinitronaphthalene* as lustrous flat needles, m. p. 214—216° (Found: C, 52·2; H, 3·7. $C_{12}H_{10}N_2O_6$ requires C, 51·8; H, 3·6%), $\nu_{max.}$ 708, 732, 745, 775, 786, 845s, 868s, 892s, 920, 965s, 1020, 1053s, 1100, 1130, 1263, 1280s, 1305, 1340vs, 1370, 1430s, 1480s, 1520vs, 1540vs, 1610, 1635 cm.$^{-1}$. It was distinguished from the compound under (*b*) by its pale colour, by mixed m. p. which was below 180°, and absence of colour with sodium hydroxide solution.

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