1046. 1,2-*Quinones from Derivatives of* 2,7-*Dihydroxynaphthalene.*

By F. Bell.

1,2-Naphthaquinones are obtained by the action of nitric acid on derivatives of 2,7-dihydroxynaphthalene. Halogen atoms substituted into certain 2,7-dihydroxy- and 2,7-dimethoxy-naphthalenes are remarkably mobile.

Fries and Schimmelschmidt [1] obtained a number of 1,2-naphthaquinones by oxidation of derivatives of 2-naphthol but the only related observation in the 2,7-dihydroxynaphthalene series is that of Wilson,[2] who obtained in very minute yield the quinone (I) by the oxidation of 1,6-dibromo-2,7-dimethoxynaphthalene with chromium trioxide. It is now found that this compound can be prepared in good yield and in higher purity by use of nitric acid as the oxidising agent.

As dichloro-2,7-dimethoxy- and -dihydroxy-naphthalene are believed [2] to have the halogen atoms in positions 1,6 it was expected that with nitric acid they would yield products analogous to (I), but this was not so. Dichloro-2,7-dimethoxynaphthalene with nitric acid gave a yellow compound, which when heated or crystallised from boiling acetic acid lost nitrosyl chloride and gave a red 1,2-quinone containing only one atom of chlorine. These reactions would be most readily explained if the starting material were 1,8-dichloro-2,7-dimethoxynaphthalene, the yellow intermediate were (II), and the final product (III). Dichloro-2,7-dihydroxynaphthalene behaved similarly in that one chlorine atom was expelled but two nitro-groups simultaneously entered the molecule to give a product most simply formulated as (IV), having regard to the fact [3] that 1,2-naphthaquinone undergoes nitration in position 3. It was then essential to establish the constitution of these dichloro-compounds by synthesis. 1-Chloro-2,7-dimethoxy-8-nitronaphthalene [4] was reduced to the corresponding amine in about 30% yield; rather surprisingly a small amount of 1-chloro-2,7-dimethoxynaphthalene was also produced in this reaction. From the amine there was obtained by the Sandmeyer reaction 1,8-dichloro-2,7-dimethoxynaphthalene, although in very small yield. This was identical with the compound obtained by the dichlorination of 2,7-dimethoxynaphthalene, or by the methylation of dichloro-2,7-dihydroxynaphthalene, and structures (II) and (III) are regarded as confirmed.

When 1-bromo-2,7-dimethoxynaphthalene was chlorinated there was produced a

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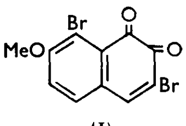
[1] Fries and Schimmelschmidt, *Annalen*, 1930, **484**, 245.

[2] Wilson, *Tetrahedron*, 1960, **11**, 256.

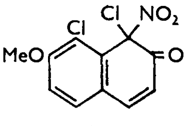
[3] Zincke and Noack, *Annalen*, 1897, **295**, 1; Fieser and Ames, *J. Amer. Chem. Soc.*, 1927, **49**, 2604.

[4] Bell and Gorrie, *J.*, 1961, 4258.

product of somewhat indefinite m. p. Repeated recrystallisation from acetic acid gave material the infrared spectrum of which was essentially identical with that of the product of monobromination of 1-chloro-2,7-dimethoxynaphthalene. This compound gave with nitric acid a naphthaquinone very similar to (I) and regarded as having structure (V). The latter could arise in two ways, (*a*) from 8-bromo-1-chloro-2,7-dimethoxynaphthalene by migration of the bromine atom at some stage in the reaction, or (*b*) directly from 6-bromo-1-chloro-2,7-dimethoxynaphthalene. With regard to process (*a*) several analogous examples of migration of a bromo-substituent in phenols and phenolic ethers under the action of nitric acid are known,[5] *e.g.*, (VI) ⟶ (VII).[6] On the other hand, process (*b*) presupposes a migration of the bromine atom in the course of the chlorination of 1-bromo-2,7-dimethoxynaphthalene, a change which might be regarded as similar to the isomerization of 1,3- to 1,6-dibromo-2,7-dihydroxynaphthalene.[7] The halogen atoms in these naphthalene derivatives are very mobile. Wilson has described the transbromination of 1,6-dibromo-2,7-dihydroxynaphthalene [2] and it is now found that when 1,8-dichloro-2,7-dimethoxynaphthalene is boiled in ethanol containing hydrogen bromide it undergoes conversion into the above bromo-1-chloro-2,7-dimethoxynaphthalene. Since this bromo-1-chloro-compound is not reconverted into the 1,8-dichloro-compound by boiling ethanolic hydrogen chloride and is unaffected by reducing agents (which normally remove α-bromine atoms [7]), the constitution 6-bromo-1-chloro-2,7-dimethoxynaphthalene appears to be indicated.* This provisional conclusion is adopted in the Experimental part.



(I)



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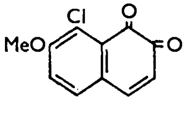

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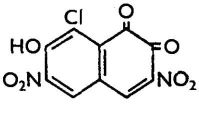

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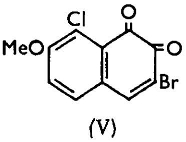

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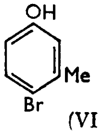

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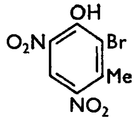
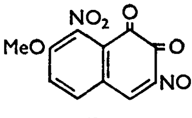


(VII)



(VIII)

1-Chloro-2,7-dimethoxy-8-nitronaphthalene with nitric acid suffered loss of halogen to give a 1,2-quinone, probably (VIII). It has already been recorded that 1-bromo-2,7-dimethoxynaphthalene with nitric acid suffers replacement of bromine to give trinitro-2,7-dimethoxynaphthalene.[4]

EXPERIMENTAL

Interaction of 1,6-*Dibromo*-2,7-*dimethoxynaphthalene with Nitric Acid*.—Concentrated nitric acid (1 c.c.) in acetic acid (3 c.c.) was added to a warm solution of the compound [7,8] (1 g.) in acetic acid (10 c.c.). In a few minutes the liquid set to a red paste of fine needles of 3,8-dibromo-7-methoxy-1,2-naphthaquinone (I), m. p. 268° (decomp.), unchanged after recrystallisation from a large bulk of acetic acid (Found: C, 38·4; H, 1·7; Br, 46·4; OMe, 9·1. Calc. for $C_{11}H_6Br_2O_3$: C, 38·1; H, 1·7; Br, 46·2; OMe, 9·0%). Wilson [2] gives 244° as the m. p. of this naphthaquinone prepared by the oxidation of 1,6-dibromo-2,7-dimethoxynaphthalene by chromic acid. This experiment was repeated and the product had the m. p. given by Wilson. I am indebted to Dr. D. M. W. Anderson for the report that the infrared spectra of the two samples are essentially identical. The quinone gave a blue-green colour with

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* The infrared spectrum closely resembled in pattern that of 1,6-dibromo-2,7-dimethoxynaphthalene and differed markedly from that of 1,8-dichloro-2,7-dimethoxynaphthalene.

[5] Nightingale, *Chem. Rev.*, 1947, **40**, 117.

[6] Sen, *Proc. Nat. Acad. Sci. India*, 1939, **9**, 89; *Chem. Abstr.*, 1941, **35**, 1038.

[7] Cooke, Johnson, and Owen, *Austral. J. Chem.*, 1960, **13**, 256.

[8] Wilson, *Tetrahedron*, 1958, **3**, 236.

concentrated sulphuric acid, and readily condensed with *o*-phenylenediamine in acetic acid to give a *quinoxaline*, which recrystallised from acetic acid in canary-yellow needles, m. p. 215° (Found: C, 48·7; H, 2·2. $C_{17}H_{10}Br_2N_2O$ requires C, 48·8; H, 2·4%).

Interaction of 1,8-*Dichloro*-2,7-*dimethoxynaphthalene with Nitric Acid.*—(*a*) Concentrated nitric acid (1 c.c.) in acetic acid (2 c.c.) was added to a hot solution of the compound (1 g.) in acetic acid (10 c.c.). On cooling there separated bright yellow 1,8-*dichloro*-1,2-*dihydro*-7-*methoxy*-1-*nitro*-2-*oxonaphthalene* (II), m. p. 130° (decomp.) (Found: C, 45·7; H, 2·5; Cl, 23·4; OMe, 10·7. $C_{11}H_7Cl_2NO_4$ requires C, 45·8; H, 2·4; Cl, 24·6; OMe, 10·6%). It was easily soluble in chloroform, benzene, and ethyl acetate, but slowly crystallised from solution in hot methanol without change in m. p. Above 130° this compound gave 8-*chloro*-7-*methoxy*-1,2-*naphthaquinone* (III) which formed bright red needles, m. p. 216° (decomp.), from acetic acid (Found: C, 59·3; H, 2·9; Cl, 16·0; OMe, 14·1. $C_{11}H_7ClO_3$ requires C, 59·3; H, 3·1; Cl, 16·0; OMe, 13·9%) and gave a deep green colour with concentrated sulphuric acid.

(*b*) The dimethoxy-compound was introduced slowly into fuming nitric acid; it first gave a brilliant permanganate colour. The resultant solution was poured into water and the red precipitate recrystallised from acetic acid to yield maroon crystals of 8-*chloro*-7-*methoxy*-3(?)-*nitro*-1,2-*naphthaquinone*, m. p. 262° (decomp.) (Found: C, 49·3; H, 2·2. $C_{11}H_6ClNO_5$ requires C, 49·3; H, 2·2%). This compound gives a purple colour with concentrated sulphuric acid and a *quinoxaline*, yellow needles, m. p. 237—240°, with *o*-phenylenediamine in acetic acid (Found: C, 59·7; H, 3·0. $C_{17}H_{10}ClN_3O_3$ requires C, 60·1; H, 2·9%). This quinoxaline gave a deep green colour with concentrated sulphuric acid.

1,8-*Dichloro*-2,7-*dihydroxynaphthalene.*—Sulphuryl chloride (3·5 c.c.) in chloroform was added dropwise to a stirred suspension of 2,7-dihydroxynaphthalene (3·2 g.) in chloroform (20 c.c.). After the vigorous reaction the mixture was warmed on a steam bath and filtered from the main crop (4 g.; m. p. 178—186°). The filtrate, on standing, deposited a further small crop of the same material. One crystallisation from acetic acid raised the m. p. to 187—189°. With methyl sulphate and sodium hydroxide the product readily gave 1,8-dichloro-2,7-dimethoxynaphthalene, m. p. 144° alone or mixed with the product of dichlorination of 2,7-dimethoxynaphthalene (this confirms Wilson's observation [2]). Use of 6 c.c. of sulphuryl chloride in the above preparation led to an almost quantitative yield of 1,1,8-trichloro-1,2-dihydro-7-hydroxy-2-oxonaphthalene, which crystallised from ethanol in large yellow rhombs, m. p. 185° (decomp.).[9]

1,8-Dichloro-2,7-dimethoxynaphthalene was unchanged after being boiled with an ethanolic solution of hydrogen chloride for 2 hr.

Interaction of 1,8-*Dichloro*-2,7-*dihydroxynaphthalene with Nitric Acid.*—Fuming nitric acid (2 c.c.) in acetic acid (4 c.c.) was added to the compound (1 g.) in acetic acid (10 c.c.). The mixture became deep red but no crystallisation occurred even on storage. Water precipitated an orange product readily soluble in most solvents. When a solution of it in acetic acid was boiled decomposition set in with evolution of nitrosyl chloride and deposition of red crystals of 8-*chloro*-7-*hydroxy*-(?)3,5-*dinitro*-1,2-*naphthaquinone* (IV), prisms, m. p. 230° (decomp.) (from acetic acid) (Found: C, 40·2; H, 1·0. $C_{10}H_3ClN_2O_7$ requires C, 40·2; H, 1·0%). This quinone becomes black immediately it comes into contact with aqueous solvents. It gives a dichromate colour with concentrated sulphuric acid and with *o*-phenylenediamine in acetic acid a yellow *quinoxaline*, m. p. 262° (Found: C, 52·1; H, 1·6. $C_{16}H_7ClN_4O_5$ requires C, 51·8; H, 1·9%). This quinoxaline gives a dark green colour with concentrated sulphuric acid.

8-*Chloro*-2,7-*dimethoxy*-1-*naphthylamine.*—1-Chloro-2,7-dimethoxy-8-nitronaphthalene [4] (4 g.) was suspended in ethanol (50 c.c., saturated with hydrogen chloride), and stannous chloride (12 g.) was added. The whole was warmed on a steam-bath for 1 hr. during which the liquid became filled with a white precipitate. After cooling, the precipitate was filtered off and decomposed with sodium hydroxide, and the product crystallised from ethanol to yield the *base* as plates, m. p. 104—107° (1·4 g.) (Found: C, 60·0; H, 5·1. $C_{12}H_{12}ClNO_2$ requires C, 60·6; H, 5·1%). The original filtrate, on working up, gave almost black, sticky material from which a small quantity of 1-chloro-2,7-dimethoxynaphthalene was removed by steam.

1,8-*Dichloro*-2,7-*dimethoxynaphthalene.*—The above base (2·8 g.), without further purification, was dissolved in boiling hydrochloric acid (5 c.c. of concentrated acid in 25 c.c. of water), and the solution rapidly cooled to yield the hydrochloride as a paste. To this was added sodium

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[9] Bell, Gibson, and Wilson, *J.*, 1956, 2335.

nitrite (0·8 g. in 2 c.c. of water); the whole became very dark. After ¼ hr. the liquid was filtered from a considerable black slime, and the golden-yellow filtrate poured into cuprous chloride in hydrochloric acid. A yellow precipitate that was formed proved to be a copper compound, so it was separated and decomposed by boiling dilute hydrochloric acid. The product, repeatedly recrystallised from acetic acid, gave the dichloro-derivative as almost colourless needles, m. p. 144°. Dr. D. M. W. Anderson kindly confirmed that the infrared spectrum of this material was identical with that of the dichlorination product of 2,7-dimethoxynaphthalene.

6-*Bromo*-1-*chloro*-2,7-*dimethoxynaphthalene*.—(*a*) Bromine (1 mol.) in chloroform was added to a solution of 1-chloro-2,7-dimethoxynaphthalene in chloroform. Immediate evolution of hydrogen bromide occurred. The mixture was concentrated and then diluted with light petroleum to give an almost quantitative yield of the 6-*bromo-derivative*, which crystallised from ethanol in needles, m. p. 128—129° (Found: C, 47·7; H, 3·2. $C_{12}H_{10}O_2BrCl$ requires C, 47·8; H, 3·3%). This compound suffers no appreciable lowering in m. p. on admixture with 1,6-dibromo-2,7-dimethoxynaphthalene, m. p. 128°, supporting the view that the two have identical orientations. (*b*) Hydrobromic acid (15 c.c.; *d* 1·7) was added during 2 hr. to a boiling solution of 1,8-dichloro-2,7-dimethoxynaphthalene (2 g.) in ethanol (50 c.c.). On cooling there separated 0·9 g. of unchanged material. The filtrate on concentration yielded the bromochloro-compound, m. p. and mixed m. p. 128—129°, but considerably depressed on addition of 1,8-dichloro-2,7-dimethoxynaphthalene (Found: C, 47·7; H, 3·3%). (*c*) Sulphuryl chloride (1 mol.) in chloroform was added to a solution of 1-bromo-2,7-dimethoxynaphthalene in chloroform and the mixture concentrated and diluted with light petroleum. The precipitate recrystallised from methanol as needles, m. p. 127° with previous sintering (Found: C, 47·7; H, 3·1%). The infrared spectrum coincided with that of the compound described under (*a*).

In the preparation of 1-bromo-2,7-dimethoxynaphthalene by conducting bromine vapour, in a current of carbon dioxide, into a chloroform solution of 2,7-dimethoxynaphthalene, the leading-in tube became filled with a white solid. This was purified by recrystallisation from pyridine and formed needles, m. p. 193—196° (Found: C, 28·7; H, 1·6; Br, 62·7. Calc. for $C_{12}H_8Br_4O_2$: C, 28·6; H, 1·6; Br, 63·5%) (contrast Cooke, Johnson, and Owen [7]).

Interaction of 6-*Bromo*-1-*chloro*-2,7-*dimethoxynaphthalene with Nitric Acid*.—Fuming nitric acid (2 c.c.) in acetic acid was added to a warm solution of the compound (1 g.) in acetic acid (10 c.c.). The dark solution gradually deposited yellow crystals (Found: C, 36·9; H, 1·7%), which decomposed on slight warming or in boiling acetic acid, to give 3-*bromo*-8-*chloro*-7-*methoxynaphthaquinone* (V), needles (from acetic acid), m. p. 260° (decomp.) (Found: C, 44·2; H, 2·0; Cl, 11·6; Br, 25·9. $C_{11}H_6BrClO_3$ requires C, 43·8; H, 2·0; Cl, 11·8; Br, 26·5. Calc. for $C_{11}H_6BrClO_3,HNO_3$: C, 36·2; H, 1·9%). This compound gives a blue-green colour with concentrated sulphuric acid, and with *o*-phenylenediamine in acetic acid a *quinoxaline*, which recrystallised from acetic acid in canary-yellow needles, m. p. 214—216° (Found: C, 54·4; H, 2·5. $C_{17}H_{10}BrClN_2O$ requires C, 54·6; H, 2·7%).

Interaction of 1-*Chloro*-2,7-*dimethoxy*-8-*nitronaphthalene with Nitric Acid*.—The compound [4] (1 g.) was slowly introduced into fuming nitric acid (5 c.c.), and the resultant solution poured in water. The product after recrystallisation from acetic acid formed maroon needles, m. p. 262° (decomp.), of 3(?),8-*dinitro*-7-*methoxy*-1,2-*naphthaquinone* (VIII) (Found: C, 47·7; H, 2·0; N, 9·9. $C_{11}H_6N_2O_7$ requires C, 47·5; H, 2·2; N, 10·1%). This compound gives a cherry-red colour with concentrated sulphuric acid.

1-Chloro-2,7-dimethoxy-8-nitronaphthalene was unchanged after several hours in hot ethanolic hydrogen bromide.

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