Hydroxybenzotropones. Part II. The Isomeric* 1 : 2 : 3 : 4-*Tetrahydro*-2 : 3-*methylene*-1 : 4-*dioxonaphthalenes.*

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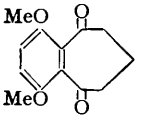
[Reprint Order No. 6172.]

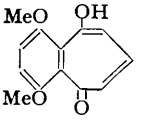
Bromination of diketones of type (I) and treatment of the products with pyridine gives *cyclo*propano-diketones of the type (III). The structure (III; R = Br) is established by hydrogenation, degradation, and spectroscopic evidence.

Bromomethylnaphthaquinones can be prepared by reaction of the corresponding methylnaphthaquinones with *N*-bromosuccinimide.

One of the unsuccessful procedures used in efforts to convert the ether (I) into the hydroxybenzotropone (II) was bromination–dehydrobromination (see Part I *). This led to a number of bromo-compounds isomeric with the desired hydroxybenzotropones. The structures of these compounds are now considered.



(I)



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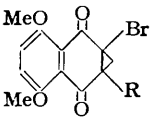

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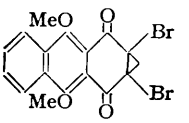


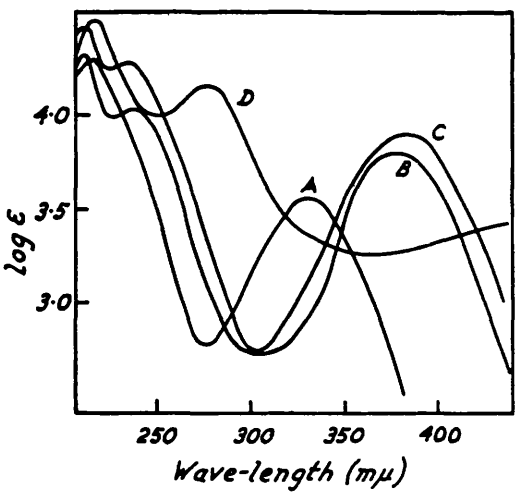
(IV)

Bromination of the ether (I) with 2 mols. of bromine in glacial acetic acid gave a dibromo-derivative which on treatment with pyridine lost the elements of hydrogen bromide to give a pale yellow, alkali-insoluble product, $C_{13}H_{11}O_4Br$. The same substance was obtained in lower yield by using *N*-bromosuccinimide, but we were unable to produce a bromine-free compound. Similarly, use of 4 mols. of bromine led to an unstable tetrabromo-diketone which lost bromine when treated with pyridine to yield a second yellow, alkali-insoluble compound, $C_{13}H_{10}O_4Br_2$. The two products were obviously closely related (the ultraviolet absorption curves are annexed) and, since dehydrogenation had occurred in their formation from the ether (I), they were regarded as (III; R = H and Br). This has now been established. Debromination with pyridine, referred to above, appears to be new but an analogous reaction was observed by Ingold (*J.*, 1921, **119**, 305) who found that reaction of αα′-dibromoglutaric ester with alcoholic potassium hydroxide gave a mixture in which bromine-free *cyclo*propane derivatives predominated. Reaction of the phenol (I; OH in place of OMe) with 2 mols. of bromine gave two bromo-derivatives. Treated separately with pyridine they afforded a mono- and a di-bromodihydroxy-diketone from which the compounds (III; R = H and Br) were obtained by methylation. The dibromo-diketone (III; R = Br) was examined in detail.

* Part I, preceding paper.

Determination of Structure.—The bromine atoms. As the bromine atoms in the compound (III; R = Br) were completely stable to alkaline hydrolysis they could either be at bridgehead positions (as shown) or be located *ortho* to the methoxyl groups. By condensing glutaric acid with 2 : 3-dichloro- and with 2 : 3-dimethyl-quinol, and methylation of the products, two further diketones of type (I), but having positions 6 and 7 blocked, were obtained. Bromination of these diketones with 4 mols. of bromine and treatment with pyridine again yielded dibromo-compounds in which the bromine atoms must be attached to the α-carbon atoms. Structure (III) therefore appeared to be correct as far as the bromine atoms were concerned. Some further evidence is mentioned below.

The cyclo*propane ring.* The existence of the *cyclo*propane ring was demonstrated by reactions in which the ring was opened in both possible ways. Catalytic hydrogenation over Adams catalyst led to ring fission and removal of the bromine atoms. After uptake of 3 mols. of hydrogen the original diketone (I) was isolated. Reaction of the compound (III; R = Br) with hydrobromic acid in boiling acetic acid resulted in opening of the *cyclo*propane ring and demethylation to a product $C_{11}H_6O_4Br_2$. A closely related substance



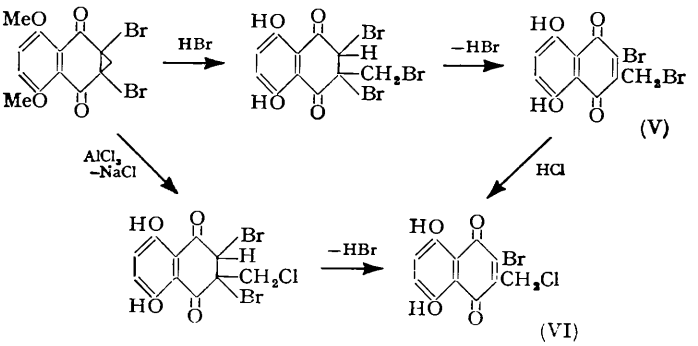
A, 1′ : 4′-*Dimethoxy*-1 : 2-*benzo*cyclo*heptene*-3 : 7-*dione* (I).
B, 2-*Bromo*-1 : 2 : 3 : 4-*tetrahydro*-5 : 8-*dimethoxy*-2 : 3-*methylene*-1 : 4-*dioxonaphthalene* (III; R = H).
C, 2 : 3-*Dibromo*-1 : 2 : 3 : 4-*tetrahydro*-5 : 8-*dimethoxy*-2 : 3-*methylene*-1 : 4-*dioxonaphthalene* (III; R = Br).
D, *Bromonaphthazarin dimethyl ether* (VIII).

Solvent: methanol.

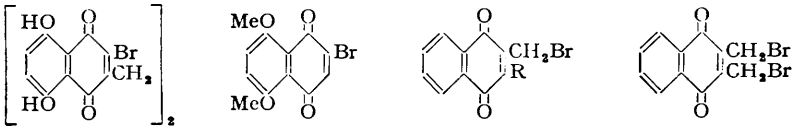
$C_{11}H_6O_4BrCl$, was obtained by fusion in sodium chloride–aluminium chloride at 180°. The latter product was also obtained by refluxing the former in hydrochloric–acetic acid. Mixed melting point determinations of the two compounds showed no depression; this was also true of their diacetates. The compounds were readily recognised as naphthazarins by their deep cornflower-blue solutions in aqueous sodium hydroxide and sodium carbonate, by the formation of diacetates but not methyl ethers, and by their light absorption. The formula $C_{11}H_6O_4Br_2$ corresponds to a dibromomethylnaphthazarin. If the initial bromination of the ether (I) had taken place partly in the benzenoid ring a reasonable structure for this product would be 6 : 7-dibromo-2-methylnaphthazarin. This was synthesised by the condensation of dibromomaleic anhydride with toluquinol. The two compounds were different although their ultraviolet absorption spectra were very similar. This further established the location of the bromine atoms in the compound (III; R = Br). The most probable formulation of this new dibromonaphthazarin therefore seemed to be 2-bromo-3-bromomethylnaphthazarin (V) which could arise as shown.

Reduction of the quinone (V) to 2-bromo-3-methylnaphthazarin would be a convenient way to establish its structure. It has been shown (Thomson, *J.*, 1953, 1196) that catalytic reduction of chloromethylnaphthaquinones at a palladium catalyst gives rise (after reoxidation) to diquinones, but we now find that use of a platinum catalyst leads to the corresponding methylquinone, *e.g.*, 2-chloromethyl-3-methyl-1 : 4-naphthaquinone reduced with hydrogen and Adams catalyst and then reoxidised gave 2 : 3-dimethyl-1 : 4-naphthaquinone. However this procedure was not successful with the compound (V); the product

was not 2-bromo-3-methylnaphthazarin but an unidentified naphthazarin of high m. p. and low solubility, probably another diquinone (VII?). Reduction by the stannous chloride method (Bruce and Thomson, *J.*, 1952, 2759) to obtain a simple β-hydro-



naphthazarin again gave a more complex compound of high m. p. which could be oxidised to a naphthazarin, probably similar to (VII?). Direct synthesis of the quinones (V) and (VI) was then explored. Chloromethylation and bromomethylation of bromonaphthazarin dimethyl ether (VIII) seemed a feasible route but reaction in formaldehyde–hydrochloric



acid–acetic acid (Thomson, *loc. cit.*) gave only a little 2 : 3-dichloronaphthazarin dimethyl ether. Bromomethylation of quinones has only been achieved hitherto in very low yield by the peroxide alkylation method (Fieser *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 3203), but 2-bromomethyl-3-methyl-1 : 4-naphthaquinone (IX; R = Me) was readily obtained from 2-methyl-1 : 4-naphthaquinone in formaldehyde–hydrobromic acid–acetic acid, and was converted into the chloromethyl analogue with hydrochloric acid. We could not extend this procedure to the bromomethylation of the quinone (VIII) and Kubiezek and Neugebauer's method (*Monatsh.*, 1950, **81**, 917) was also unsuccessful. The failure to bromomethylate and chloromethylate bromo(and chloro)naphthazarin dimethyl ether is probably due to salt formation with the halogen acid (Bruce and Thomson, *J.*, 1955, 1089). Finally a general synthesis of bromomethylnaphthaquinones was found in the reaction of methylnaphthaquinones with *N*-bromosuccinimide. In this way the compounds (IX; R = H and Br) were obtained from 2-methyl- and 3-bromo-2-methyl-1 : 4-naphthaquinone; and 2 : 3-dimethyl-1 : 4-naphthaquinone afforded the dibromide (X). The reaction failed with methylnaphthazarin, but 2-bromo-3-methylnaphthazarin diacetate yielded 2-bromo-3-bromomethylnaphthazarin diacetate, hydrolysis of which gave the desired dibromoquinone (V). This established the structure (V) and hence (III; R = Br). The structure (VI) for the bromochloro-product obtained by aluminium chloride degradation of the compound (III; R = Br) is based on the fact that it can be obtained from the dibromo-compound (V) by reaction with hydrochloric acid in acetic acid; and the monobromo-compound (IX; R = Me) also gives the corresponding chloromethyl compound under the same conditions, whereas 3-bromo-2-methylnaphthazarin is unaffected.

Spectroscopic evidence. Infrared examination of the compounds (III; R = Br) and (IV) supported the chemical evidence described above. No infrared spectra for *cyclo*propane compounds of this complexity are available but from an examination of many simpler compounds, including *cyclo*propano-ketones, Slabey (*J. Amer. Chem. Soc.*, 1954, **76**, 3604) has shown that a band in the 9·5—10·0-μ region is characteristic of a *cyclo*propane ring. The diketone (III; R = Br) showed absorption bands at 988 and 1058 cm.$^{-1}$, and

the analogue (IV) at 990 and 1032 cm.$^{-1}$, but this is not reliable evidence of the existence of a *cyclo*propane ring in these compounds since the diketone (I) shows a weak band at 990 cm.$^{-1}$ and stronger bands at 1016, 1045, and 1060 cm.$^{-1}$, and absorption in this region appears to be general for such *peri*-methoxy cyclic ketones (unpublished work). The infrared spectra of a number of organic bromides have been examined in the 14·5—19·5-μ region by Mortimer, Blodgett, and Daniels (*J. Amer. Chem. Soc.*, 1947, **69**, 822) who found that aliphatic bromides showed two bands, one in the region 515—570 cm.$^{-1}$, the other in the region 645—690 cm.$^{-1}$; the three aliphatic dibromides studied showed no characteristic C–Br bands outside the range 554—652 cm.$^{-1}$. Bromobenzene and α-bromonaphthalene give bands at 678 and 648 cm.$^{-1}$ respectively. The diketone (III; R = Br) shows two bands in this region, one at 551 and the other at 700 cm.$^{-1}$ (which seems too high for a C–Br vibration), and the compound (IV) gives a band at 576 cm.$^{-1}$. From this it appears that the two bromine atoms in both compounds are attached to the aliphatic ring in agreement with the chemical evidence.

These compounds also exemplify the ability of *cyclo*propane rings to conjugate with neighbouring double bonds. This is seen in the appearance of colour on passing from (I) to (III) and the shift in the ultraviolet absorption produces a curve intermediate between those of (I) and bromonaphthazarin dimethyl ether (see Figure).

Experimental

2-Bromo-1 : 2 : 3 : 4-tetrahydro-5 : 8-dimethoxy-2 : 3-methylene-1 : 4-dioxonaphthalene (III; R = H).—To 1′ : 4′-dimethoxy-1 : 2-benzo*cyclo*heptene-3 : 7-dione (1·17 g.), dissolved in glacial acetic acid (10 ml.), was added slowly with stirring, bromine (0·53 ml., 2 mols.) in glacial acetic acid (2 ml.). Evolution of hydrogen bromide soon started and a pale yellow solid separated. After 5 hr., the dibromo-derivative was collected and had m. p. 168—170° (1·82 g.). This product (1 g.) was dissolved in hot pyridine (8 ml.) and set aside overnight. The mixture was then poured into dilute hydrobromic acid, and the precipitate collected. Crystallisation first from aqueous acetic acid and then from benzene (charcoal) afforded pale yellow needles, m. p. 208° (decomp.) (0·7 g., 88%) (Found: C, 50·5; H, 3·7; Br, 25·8. $C_{13}H_{11}O_4Br$ requires C, 50·15; H, 3·55; Br, 25·75%). Light absorption: max. at 210, 235, and 380 mμ (log ε 4·32, 4·03, and 3·79 respectively) in MeOH.

2 : 3-Dibromo-1 : 2 : 3 : 4-tetrahydro-5 : 8-dimethoxy-2 : 3-methylene-1 : 4-dioxonaphthalene (III; R = Br).—The procedure was the same as above except that bromine (1·1 ml., 4 mols.) was used. The intermediate tetrabromo-derivative was a bright yellow solid, m. p. 224° (decomp.) (2·5 g.) (Found: Br, 56·0. $C_{13}H_{10}O_4Br_4$ requires Br, 58·0%). The final *product* crystallised from benzene (charcoal) in bright yellow needles, m. p. 251° (decomp.) (0·8 g., 45%) (Found: C, 39·7; H, 2·7; Br, 40·2. $C_{13}H_{10}O_4Br_2$ requires C, 40·0; H, 2·55; Br, 41·0%). Light absorption: max. at 210, 232, and 383 mμ (log ε 4·48, 4·26, and 3·90 respectively) in MeOH.

2-Bromo-1 : 2 : 3 : 4-tetrahydro-5 : 8-dihydroxy-2 : 3-methylene-1 : 4-dioxonaphthalene.—Bromine (1·1 ml., 4 mols.) in glacial acetic acid (2 ml.) was added with stirring to a solution of 1′ : 4′-dihydroxy-1 : 2-benzo*cyclo*heptene-3 : 7-dione (1 g.) in the same solvent (30 ml.). After 5 days, the yellow crystals which had separated were collected (m. p. 186°). Dilution of the filtrate with water afforded a red precipitate (m. p. 50°). The solid, m. p. 186°, was dissolved in hot pyridine (5 ml.), set aside for 12 hr., then poured into dilute hydrobromic acid, and the precipitate crystallised from benzene–light petroleum (b. p. 80—90°) to give the *bromo-derivative* as yellow needles, m. p. 135° (Found: C, 46·75; H, 2·45; Br, 28·1. $C_{11}H_7O_4Br$ requires C, 46·65; H, 2·45; Br, 28·3%). The bromo-derivative, m. p. 50°, gave, after the same treatment with pyridine, *2 : 3-dibromo-1 : 2 : 3 : 4-tetrahydro-5 : 8-dihydroxy-2 : 3-methylene-1 : 4-dioxonaphthalene*, as orange-yellow needles, m. p. 174° (from light petroleum, b. p. 100—120°) (Found: C, 36·65; H, 1·7; Br, 43·8. $C_{11}H_6O_4Br_2$ requires C, 36·45; H, 1·65; Br, 44·2%). Methylation of these two compounds with methyl sulphate–acetone–potassium carbonate afforded the respective dimethyl ethers (III; R = H and Br).

1′ : 4′-Dihydroxynaphtho(2′ : 3′-1 : 2)cycloheptene-3 : 7-dione.—The *p-nitrophenylhydrazone* crystallised from aqueous acetic acid in orange crystals, m. p. 228° (Found: C, 64·15; H, 4·75; N, 10·8. $C_{21}H_{17}O_5N_3$ requires C, 64·45; H, 4·35; N, 10·8%).

2 : 3-Dibromo-1 : 2 : 3 : 4-tetrahydro-9 : 10-dimethoxy-2 : 3-methylene-1 : 4-dioxoanthracene (IV).—To 1′ : 4′-dimethoxynaphtho(2′ : 3′-1 : 2)*cyclo*heptene-3 : 7-dione (0·14 g.), dissolved in glacial acetic acid (7 ml.), was added bromine (0·05 ml.) in the same solvent (1 ml.). After 6 days, the

solution was diluted with water, and the precipitate collected (m. p. 80°). Treatment with pyridine, as described above, gave the *product* as pale yellow needles, m. p. 147° (from aqueous methanol) (70 mg.) (Found: C, 46·6; H, 3·0. $C_{17}H_{12}O_4Br_2$ requires C, 46·35; H, 2·75%).

2′ : 3′-*Dichloro*-1′ : 4′-*dihydroxy*-1 : 2-*benzo*cyclo*heptene*-3 : 7-*dione*.—This was prepared from 2 : 3-dichloroquinol and glutaric acid by the procedure of Bruce, Sorrie, and Thomson (*J.*, 1953, 2403). The *diketone* crystallised from light petroleum (b. p. 100—120°) in orange-yellow leaflets, m. p. 204° (16%). Sublimation *in vacuo* gave bright yellow crystals (Found: C, 48·0; H, 3·05; Cl, 25·5. $C_{11}H_8O_4Cl_2$ requires C, 48·0; H, 3·0; Cl, 25·8%). The *dimethyl ether* crystallised from aqueous acetic acid in needles, m. p. 135° (Found: C, 51·3; H, 4·15. $C_{13}H_{12}O_4Cl_2$ requires C, 51·15; H, 3·95%).

2 : 3-*Dibromo*-6 : 7-*dichloro*-1 : 2 : 3 : 4-*tetrahydro*-5 : 8-*dimethoxy*-2 : 3-*methylene*-1 : 4-*dioxonaphthalene*.—Bromination of the above dimethyl ether with bromine (4 mols.) gave a solid, m. p. 178—180°. Treatment with pyridine gave the desired *product* which crystallised from light petroleum (b. p. 80—90°) in pale yellow, slender, needles, m. p. 211° (decomp.) (Found: C, 34·1; H, 1·55. $C_{13}H_8O_4Br_2Cl_2$ requires C, 34·0; H, 1·75%).

1′ : 4′-*Dihydroxy*-2′ : 3′-*dimethyl*-1 : 2-*benzo*cyclo*heptene*-3 : 7-*dione*.—This *diketone*, prepared from 2 : 3-dimethylquinol and glutaric acid, crystallised from light petroleum (b. p. 100—120°), forming orange needles, m. p. 83° (34%) (Found: C, 66·3; H, 5·9. $C_{13}H_{14}O_4$ requires C, 66·6; H, 6·0%). The *dimethyl ether* crystallised from light petroleum (b. p. 100—120°) in cream-coloured rosettes, m. p. 84° (Found: C, 68·55; H, 6·8. $C_{15}H_{18}O_4$ requires C, 68·7; H, 6·9%).

2 : 3-*Dibromo*-1 : 2 : 3 : 4-*tetrahydro*-5 : 8-*dimethoxy*-6 : 7-*dimethyl*-2 : 3-*methylene*-1 : 4-*dioxonaphthalene*.—The initial bromination *product* had m. p. 145°. Treatment of this with pyridine afforded an oily solid which was washed with ether and then crystallised from light petroleum (b. p. 100—120°) to give stout needles, m. p. 165° (47%) (Found: C, 42·95; H, 3·35; Br, 37·9. $C_{15}H_{14}O_4Br_2$ requires C, 43·05; H, 3·35; Br, 38·3%).

Reactions of 2 : 3-*Dibromo*-1 : 2 : 3 : 4-*tetrahydro*-5 : 8-*dimethoxy*-2 : 3-*methylene*-1 : 4-*dioxonaphthalene*.—(a) *Hydrogenation*. The dione (1 g.), dissolved in glacial acetic acid, was hydrogenated over Adams catalyst (50 mg.). After the absorption of 3 mols. of hydrogen, the catalyst was filtered off and the solvent evaporated under reduced pressure. The oily residue solidified on drying *in vacuo* and was crystallised from light petroleum (b. p. 100—120°) to give 1′ : 4′-dimethoxy-1 : 2-benzo*cyclo*heptene-3 : 7-dione (0·35 g.), m. p. and mixed m. p. 149°.

(b) *With hydrobromic acid*. To a boiling solution of the dione (0·5 g.) in glacial acetic acid (20 ml.), was added hydrobromic acid (3 ml.; 48%). After being heated for 20 min.—the colour had changed to deep violet—the mixture was poured into water and the precipitate collected. Crystallisation from light petroleum (b. p. 100—120°) gave brown, lustrous plates of 2-*bromo*-3-*bromomethylnaphthazarin*, m. p. 149° (0·15 g.) (Found: C, 36·2; H, 1·6; Br, 44·3. $C_{11}H_6O_4Br_2$ requires C, 36·45; H, 1·65; Br, 44·0%). The *diacetate* crystallised from light petroleum (b. p. 100—120°) as maroon crystals, m. p. 206° (Found: C, 39·7; H, 2·2; Br, 35·9. $C_{15}H_{10}O_6Br_2$ requires C, 39·5; H, 2·2; Br, 35·9%).

(c) *With fused sodium chloride–aluminium chloride*. To a molten mixture of sodium chloride (3 g.) and anhydrous aluminium chloride (12 g.) at 140° was added the dione (0·7 g.). After being heated for 2 min. at 180° the mixture was cooled and decomposed with dilute hydrochloric acid (180 ml.; 2 : 1). The precipitate was collected and crystallised from light petroleum (b. p. 100—120°) to give 2-*bromo*-3-*chloromethylnaphthazarin* as dark needles with a green sheen, m. p. 154° (0·32 g.) (Found: C, 41·85; H, 2·0; Hal, 36·1. $C_{11}H_6O_4BrCl$ requires C, 41·6; H, 1·9; Hal, 36·4%). This product was also obtained by passing a stream of dry hydrogen chloride through a refluxing solution of 2-bromo-3-bromomethylnaphthazarin in glacial acetic acid for 6 hr. The *diacetate* crystallised from light petroleum (b. p. 100—120°) in orange crystals, m. p. 199° (Found: C, 44·75; H, 2·75; Hal, 27·8. $C_{15}H_{10}O_6BrCl$ requires C, 44·85; H, 2·5; Hal, 28·8%).

6 : 7-*Dibromo*-2-*methylnaphthazarin*.—This *quinone* was prepared by condensation of toluquinol and dibromomaleic acid in molten sodium chloride–aluminium chloride. Crystallisation from light petroleum (b. p. 100—120°) afforded golden-brown plates, m. p. 160° (27%) (Found: C, 36·35; H, 1·6; Br, 43·5. $C_{11}H_6O_4Br_2$ requires C, 36·45; H, 1·65; Br, 44·0%). Reduction with acid stannous chloride gave β-hydromethylnaphthazarin, m. p. and mixed m. p. 160° (Bruce and Thomson, *loc. cit.*).

Reduction of 2-*Chloromethyl*-3-*methyl*-1 : 4-*naphthaquinone*.—The quinone (0·5 g.), dissolved in glacial acetic acid (15 ml.), was hydrogenated over Adams catalyst (0·1 g.). After the absorption of 2 mols. of hydrogen, the catalyst was filtered off and washed with hot solvent.

To the combined filtrates a solution of chromium trioxide (0·2 g.) in water (2 ml.) was added, and the mixture heated for 20 min. on a steam-bath and poured into water. The yellow precipitate crystallised from aqueous acetic acid in lemon-yellow needles of 2 : 3-dimethyl-1 : 4-naphthaquinone (0·25 g.), m. p. and mixed m. p. 120°.

2-Bromomethyl-3-methyl-1 : 4-naphthaquinone.—A solution of 2-methyl-1 : 4-naphthaquinone (3 g.), acetic acid (35 ml.), and formaldehyde (9 ml.; 36%) was coooled to 0° and a stream of hydrogen bromide passed through it for 45 min. The solution became red and a solid separated. Next morning the solid was collected and crystallised from ethanol in yellow needles, m. p. 131° (43%) (Fieser *et al., loc. cit.*, report m. p. 134°) (Found : Br, 30·2. Calc. for $C_{12}H_9O_2Br$: Br, 30·2%). This quinone (1 g.) in glacial acetic acid (20 ml.) and concentrated hydrochloric acid (10 ml.) was refluxed for 1 hr., concentrated hydrochloric acid (5 ml.) added, and the mixture refluxed for a further 30 min. and poured into water. The precipitate crystallised from aqueous alcohol in yellow needles, m. p. 106°, undepressed on admixture with 2-chloromethyl-3-methyl-1 : 4-naphthaquinone.

2-Bromonaphthazarin Dimethyl Ether.—To naphthazarin dimethyl ether (1 g.) in glacial acetic acid was added bromine (0·9 g.) in the same solvent (2 ml.). After 30 min. sodium acetate (0·5 g.) was added, and the mixture refluxed for 20 min. and poured into water. The precipitate was crystallised first from alcohol (charcoal) and then from light petroleum (b. p. 100—120°) to give orange-red needles of the *bromo-compound*, m. p. 160° (0·7 g., 50%) (Found : C, 48·9; H, 3·1; Br, 27·0. $C_{12}H_9O_4Br$ requires C, 48·5; H, 3·05; Br, 26·9%). Attempted chloromethylation of this product gave 2 : 3-*dichloronaphthazarin dimethyl ether*, orange-red needles, m. p. 237° (from alcohol). This was also obtained as follows : dry chlorine (0·15 g.) was passed into a solution of naphthazarin dimethyl ether (0·25 g.) in glacial acetic acid (10 ml.). The solution was heated for 15 min. on the steam-bath (HCl evolution), cooled, and diluted with water (50 ml.) and the scarlet precipitate collected and crystallised from alcohol. It had m. p. and mixed m. p. 237° (Found : C, 50·4; H, 2·8; Cl, 24·3. $C_{12}H_8O_4Cl_2$ requires C, 50·2; H, 2·8; Cl, 24·7%). Demethylation with sodium chloride–aluminium chloride gave 2 : 3-dichloronaphthazarin, m. p. and mixed m. p. 192° (diacetate, m. p. and mixed m. p. 231°).

2-Bromo-3-methylnaphthazarin.—Bromine (0·2 ml.) was added to a solution of 2-methylnapthazarin diacetate (1 g.) in glacial acetic acid (25 ml.). After 4 days sodium acetate was added and the mixture refluxed for 20 min., before dilution with water. The precipitate crystallised from light petroleum (b. p. 100—120°), to give the orange *bromo-diacetate*, m. p. 197° (0·9 g.) (Found : C, 49·2; H, 3·05; Br, 21·6. $C_{15}H_{11}O_6Br$ requires C, 49·05; H, 3·0; Br, 21·8%). The diacetate (0·5 g.) was refluxed for 1 hr. with concentrated hydrochloric acid (10 ml.), the mixture diluted with water, and the precipitate collected and crystallised from light petroleum (b. p. 80—90°) (charcoal) to give *2-bromo-3-methylnaphthazarin* as slender, crimson needles, m. p. 193° (0·2 g.) (Found : C, 46·8; H, 2·6; Br, 28·5. $C_{11}H_7O_4Br$ requires C, 46·65; H, 2·45; Br, 28·3%).

Bromination of Methyl-1 : 4-naphthaquinones.—General procedure. To the quinone, dissolved in dry carbon tetrachloride, was added *N*-bromosuccinimide (1 or 2 mols. as required) and a trace of benzoyl peroxide. The mixture was refluxed for 16—20 hr., the insoluble succinimide was filtered off after cooling, and the solvent removed, leaving the product. Thus *3-bromo-2-bromomethyl-1 : 4-naphthaquinone* was prepared from 3-bromo-2-methyl-1 : 4-naphthaquinone; it crystallised from methanol in yellow needles, m. p. 119° (Found : C, 40·0; H, 1·5; Br, 48·8. $C_{11}H_6O_2Br_2$ requires C, 40·0; H, 1·8; Br, 48·5%). *2-Bromomethyl-1 : 4-naphthaquinone*, from 2-methyl-1 : 4-naphthaquinone, crystallised from methanol in orange-yellow needles, m. p. 98°, which slowly darken (Found : C, 52·1; H, 2·75; Br, 30·6. $C_{11}H_7O_2Br$ requires C, 52·5; H, 2·8; Br, 31·8%). 2 : 3-Dimethyl-1 : 4-naphthaquinone afforded 2 : 3-*bisbromomethyl-1 : 4-naphthaquinone* (long, yellow needles from ethanol), m. p. 154° (Found : C, 41·6; H, 2·5; Br, 46·0. $C_{12}H_8O_2Br_2$ requires C, 41·9; H, 2·3; Br, 46·4%). The bromination of 2-bromo-3-methylnaphthazarin diacetate required 36 hr. 2-Bromo-3-bromomethylnaphthazarin diacetate was obtained and had m. p. 192°, raised to 196° on admixture with a sample prepared as previously described. Hydrolysis gave 2-bromo-3-bromomethylnaphthazarin, m. p. and mixed m. p. 149°. Re-acetylation afforded the diacetate, m. p. and mixed m. p. 205°.

We thank Dr. T. S. Robinson for the infrared data, and Coalite and Chemical Products Ltd. for a gift of 2 : 3-dimethylphenol.

THE UNIVERSITY, OLD ABERDEEN. [*Received, February 24th,* 1955.]