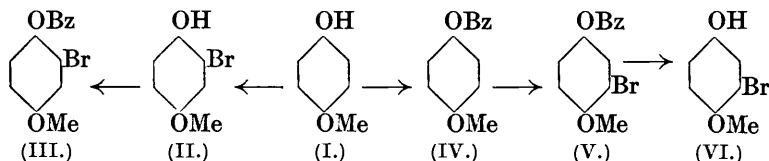


XIII.—*Bromination of Quinol Monomethyl Ether.*

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CONTRARY to the statement by Kohn and Guttmann (*Monatsh.*, 1924, 45, 575) that dibromination of quinol monomethyl ether yields only the 2 : 5-dibromoquinol monomethyl ether, it has been proved that only 30—35% of this isomeride is formed, the main product being 2 : 6-dibromoquinol monomethyl ether, as would be expected. The monobromination also is normal. It has been shown that when quinol monomethyl ether (I) is first monobrominated and then benzooylated there is formed a different substance from that obtained when it is first benzooylated and then monobrominated, and that the unbenzooylated bromoquinol monomethyl ethers are different. As the relative directive powers of the



hydroxy-, methoxy-, and benzyloxy-groups are in the order $\text{OH} > \text{OMe} > \text{OBz}$, these two bromophenols must be 2-bromoquinol monomethyl ether (II) and 3-bromoquinol monomethyl ether (VI), and the corresponding benzoyl derivatives must be represented by (III) and (V), respectively.

EXPERIMENTAL.

2-Bromoquinol Monomethyl Ether (II).—Quinol monomethyl ether (m. p. 53° , entirely free from quinol; compare Robinson and Smith, J., 1926, 393) gave a homogeneous monobromination product on treatment with excess of bromine in carbon disulphide solution.

To a solution of the quinol monomethyl ether (6.2 g.; 1 mol.) in cold carbon disulphide (140 c.c.) was slowly added, with stirring, a 20% (vol.) solution of bromine in carbon disulphide (12.5 c.c.; 1 mol.). When the yellow colour had almost disappeared, the solvent was distilled off. The residue, which solidified (m. p. $40\text{--}42^\circ$; yield, almost theoretical), was quickly recrystallised from ligroin (b. p. $60\text{--}80^\circ$) and obtained as long, colourless needles, m. p. $44\text{--}45^\circ$ (Found: C, 41.5; H, 3.6. $\text{C}_7\text{H}_7\text{O}_2\text{Br}$ requires C, 41.4; H, 3.5%). The acetyl derivative was a liquid, but the benzoyl derivative (III), obtained in 95% yield by the Schotten-Baumann method, when recrystallised from ligroin (b. p. $80\text{--}100^\circ$), melted sharply at 85°

(Found : C, 54·8; H, 3·6; Br, 26·0. $C_{14}H_{11}O_3Br$ requires C, 54·7; H, 3·6; Br, 26·0%).

3-Bromoquinol Monomethyl Ether (VI).—*4-Methoxyphenyl benzoate* (IV), obtained by the Schotten-Baumann method, melted sharply at 87° , but required recrystallisation from alcohol and from ligroin before it was pure enough for analysis (Found : C, 73·6; H, 5·4. $C_{14}H_{12}O_3$ requires C, 73·7; H, 5·3%). It could be brominated in warm acetic acid solution with an iron catalyst, or in anhydrous formic acid. The solid (11·4 g.; 1 mol.), dissolved in formic acid (75 c.c.), was warmed on a steam-bath while a solution of bromine (3·0 c.c.; 1·2 mols.) in an equal volume of formic acid was run in dropwise; the mixture was gently boiled for a few minutes until the excess of bromine was driven off, then poured into water (500 c.c.); the brown oil which formed rapidly solidified (16·1 g.). On recrystallisation from alcohol, pure *3-bromo-4-methoxyphenyl benzoate* (V), white needles, m. p. $105\cdot5^\circ$, was obtained (Found : C, 54·8; H, 3·6. $C_{14}H_{11}O_3Br$ requires C, 54·7; H, 3·6%). After hydrolysis with aqueous methyl-alcoholic sodium hydroxide, pure benzoic acid and a bromophenol (theoretical yields) were separated by means of sodium bicarbonate solution. Recrystallisation from a small volume of benzene gave long prisms, m. p. $77\text{--}78^\circ$, of *3-bromoquinol monomethyl ether* (VI) (Found : C, 41·2; H, 3·5; Br, 39·5. $C_7H_7O_2Br$ requires C, 41·4; H, 3·5; Br, 39·4%).

2 : 6-Dibromoquinol Dimethyl Ether.—In the method of preparation given by Kohn and Guttmann (*loc. cit.*, p. 582), the following improvements were introduced. Tribromophenol bromide (m. p. $137\text{--}141^\circ$), obtained from phenol (1 g. in 750 c.c. of water) and excess of bromine water, was recrystallised from warm (40°) chloroform and found always to melt at $140\text{--}141^\circ$ (decomp.) [Found : Br (by potassium iodide), 38·7. Calc. : Br, 39·0%]. It was found unnecessary to extract the crude tribromophenol bromide with alkali as recommended by Auwers and Büttner (*Annalen*, 1898, 302, 141). *2 : 6-Dibromobenzoquinone* (m. p. 132°), prepared from tribromophenol bromide and fuming nitric acid, was reduced in aqueous suspension by means of sulphur dioxide to *2 : 6-dibromoquinol*; a quantitative yield was obtained by carrying out the reduction in the cold until the red colour first produced had almost disappeared (10 minutes) and then gradually warming the mixture to 100° . Methylations of *2 : 6-dibromoquinol* (m. p. $162\text{--}163^\circ$) with sodium or potassium hydroxide solution and pure methyl sulphate gave crude products, m. p. $37\text{--}38^\circ$ (yields, 70—85%); these, after recrystallisation from methyl or ethyl alcohol, formed almost regular hexagonal plates, m. p. $38\text{--}39^\circ$. Some days later, the crystals had changed to elongated hexagonal plates, the m. p.,

53°, of which was unaltered by further recrystallisation (Found : C, 32.3; H, 2.7; Br, 53.8. Calc. : C, 32.4; H, 2.7; Br, 54.0%). The crystals melting at 53° are exactly like those described and measured by Kohn and Guttman but stated by them to melt at 56°.

Dibromination of Quinol Monomethyl Ether.—In every case, the dibromination of the quinol monomethyl ether (6.2 g.; 1 mol.) was performed at 10° in well-stirred glacial acetic acid solution (30 c.c.) by slowly adding bromine (5 c.c.; 2 mols.) in acetic acid (15 c.c.). A clean product* was obtained by distilling the hydrobromic and acetic acids during $\frac{3}{4}$ hour at 30–40°/5–10 mm. in a slow current of dry air drawn through the liquid. The residue (14.0 g.; quantitative yield) soon set to a pink, crystalline mass, m. p. 60–80°. It could be recrystallised from dilute acetic acid or from hexane; but the best method of separation was that of Kohn and Guttman, by methylation, 2 : 5-dibromoquinol dimethyl ether (Habermann, *Ber.*, 1878, 11, 1034) being insoluble in cold alcohol. Kohn and Guttman, however, failed to realise that the easily soluble 2 : 6-dibromoquinol dimethyl ether might be present in the alcoholic mother-liquor.

In a test experiment, a mixture of 2 : 5-dibromoquinol dimethyl ether (m. p. 144–145°; 1.0 g.) and the 2 : 6-isomeride (1.0 g.) was recrystallised from alcohol and gave a first crop of 0.94 g., m. p. 142–143°. Complete evaporation of the mother-liquor left 1.02 g. of crystals, m. p. 45–48°, from which by repeated recrystallisation 0.2 g. of the pure 2 : 6-isomeride, m. p. 53°, was obtained. When 1.0 g. of the soft, colourless, crystalline mixture (m. p. 43–130°) from the methylation of some dibromination product (recrystallised from hexane) was recrystallised from alcohol, only 0.4 g. of 2 : 5-dibromoquinol dimethyl ether (m. p. 142–143.5°) was obtained. After complete evaporation of the mother-liquor, clusters of well-formed, elongated hexagonal plates (0.55 g.) remained, m. p. 45–50°. Repeated crystallisation from alcohol raised the m. p. to 51–53° (Found : Br, 53.9. Calc. : Br, 54.0%). The mixed melting point with a specimen of 2 : 6-dibromoquinol dimethyl ether, m. p. 53°, was 52–53°.

In order to obtain a more accurate analysis, experiments were performed in which the entire yields of the crude bromination products were methylated, and the dimethyl ethers isolated by extraction with ether. Losses in methylation would probably be heavier in the case of the diortho-substituted 2 : 6-isomeride, so that

* The addition of ice-water to the stirred reaction mixture at first precipitates a cream-coloured oil, but the colour suddenly turns reddish-brown and then black, large amounts of tar being formed.

the proportion of 2:5-dibrominated product found would be a maximum. It is possible also that some 2:3-dibromoquinol dimethyl ether (a compound not yet known) was formed. In two experiments, 6.2 g. of quinol monomethyl ether gave 12.85 g. (yield, 87%) and 11.70 g. (yield, 79%), respectively, of mixed dibromoquinol dimethyl ethers; the quantities of the 2:5-isomeride isolated were 4.30 g. (yield, 33.5%) and 3.65 g. (yield, 31.2%), respectively.

Summary.

Quinol monomethyl ether yields on monobromination *2-bromoquinol monomethyl ether*, and on dibromination not more than 30—35% of 2:5-dibromoquinol monomethyl ether, the remainder being mostly 2:6-dibromoquinol monomethyl ether. *3-Bromoquinol monomethyl ether* also is described.

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