201. *Benzanthrones. Part III. The Synthesis of 2′-Alkyl- and 2′-Aryl-*meso*benzanthrones. The Migration from the 3′- to the 2′-Position.*

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β-Alkyl- and β-aryl-glycerol αγ-diethyl ethers are used to synthesise authentic specimens of 2′-alkyl- and 2′-aryl-*meso*benzanthrones respectively by which certain migration products have been characterised.

3′-Methyl- gives 2′-methyl-*meso*benzanthrone on heating with aluminium chloride.

The identity of the *Bz*-substituted *meso*benzanthrones has been much confused by numerous patents, and it became important in deciding between the rival theories of Meerwein and Bally and Scholl (see Part I, J., 1938, 401) to synthesise authentic specimens of 2′-substituted *meso*benzanthrones, particularly as migration can occur from the 1′- to the 2′-position (Berliner, Stein, and Trautner, U.S.P. 1,713,591; *Centr.*, 1929, **100**, II, 1074).

2′-Methyl*meso*benzanthrone has been synthesised by Lüttringhaus and Grosskinsky (D.R.-P. 482,839; *Centr.*, 1930, **101**, I, 3242) by condensing α-methylacraldehyde with anthrone. We find that 2′-alkyl- and 2′-aryl-*meso*benzanthrones are more readily obtained

by using the αγ-diethyl ethers of β-alkyl- and β-aryl-glycerols respectively (compare Warren, J., 1936, 1366) in place of the substituted aldehydes.

Two methyl*meso*benzanthrones have been isolated from crotonaldehyde and anthrone (Imray, E.P. 244,120). Sulphuric acid as a condensing agent gave a product, m. p. 113—114°, which we have identified as 3'-methyl*meso*benzanthrone (preceding paper). The other, obtained by condensation by pyridine and piperidine, followed by ring closure with aluminium chloride, has a recorded melting point 168°. A specimen kindly supplied by Farbwerke vorm. Meister Lucius und Brüning, Hoechst a./Main, for which the melting point was corrected to 164°, is identical with our 2'-methyl*meso*benzanthrone. In view of the reported migration from the 1'- to the 2'-position (Berliner, Stein, and Trautner, *loc. cit.*) it would appear that the intermediate compound was an aldol. We have found, however, that under the influence of aluminium chloride the 3'-methyl group migrates to the 2'-position and therefore the isolation of two products does not necessitate two different modes of primary condensation.

Experimental.

β-*Methylglycerol αγ-Diethyl Ether.*—This was prepared from αγ-dichloro-β-hydroxy-β-methylpropane by the method previously described (Warren, *loc. cit.*), and obtained in 60% yield as a colourless mobile liquid, b. p. 175° (Found: C, 59·0; H, 11·2. $C_8H_{18}O_3$ requires C, 59·2; H, 11·2%).

2'-*Alkyl- and* 2'-*Aryl*-meso*benzanthrones.*—Anthraquinone (9 g.; 1 mol.) in sulphuric acid was reduced to anthrone and treated with the appropriate β-substituted glycerol αγ-diethyl ether (2 mols.), the whole process being carried out as previously described in Part I (*loc. cit.*) for 1'-ethyl*meso*benzanthrone. The product after treatment with alkali was filtered and distilled with superheated steam at 200°; although there was a considerable loss of material, particularly with the aryl-substituted compound, this method of purification gave a purer product than the method described by Macleod and Allen (" Organic Syntheses," **1934**, **14**, 5). The yields given below are calculated on the anthraquinone.

2'-Methyl*meso*benzanthrone, obtained in 50% yield, crystallised from methyl alcohol in yellow needles, m. p. 165—166°, undepressed by the specimen supplied by Farbwerke vorm. Meister, Lucius und Brüning (Found: C, 88·3; H, 4·9. Calc. for $C_{18}H_{12}O$: C, 88·5; H, 4·9%). Lüttringhaus and Grosskinsky (*loc. cit.*) give m. p. 171°.

2'-*Ethyl*meso*benzanthrone*, obtained in 25% yield, crystallised from methyl alcohol in yellow needles, m. p. 117° (Found: C, 88·0; H, 5·7. $C_{19}H_{14}O$ requires C, 88·3; H, 5·5%).

2'-Phenyl*meso*benzanthrone, obtained in 5% yield, crystallised from glacial acetic acid in yellow needles, m. p. 200° (Found: C, 89·8; H, 4·7. Calc. for $C_{23}H_{24}O$: C, 90·2; H, 4·6%). Berliner, Stein, and Trautner (*loc. cit.*) give m. p. 199—200°.

Formation of 2'-*Methyl- from* 3'-*Methyl*-meso*benzanthrone by Migration.*—3'-Methyl*meso*-benzanthrone (1 g.) was added to a melt of aluminium chloride (8 g.) and sodium chloride (2 g.) and heated at 150° for 2½ hours. The cooled product was decomposed with cold dilute hydrochloric acid, and the solid collected, dried, and crystallised from methyl alcohol. The substance obtained, m. p. 115—125°, was recrystallised from methyl alcohol and then from acetic acid; it then had m. p. 164°, not depressed by 2'-methyl*meso*benzanthrone.

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