80. *Benzanthrones. Part I. The Mechanism of Bally's Reaction.*

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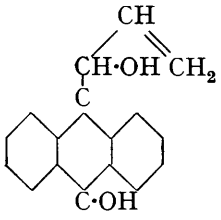
α-Ethylglycerol, which is converted into β-ethylacraldehyde by concentrated sulphuric acid, is condensed with anthranol under the conditions of Bally's reaction to give 1′-*ethyl*meso*benzanthrone*, the constitution of which is verified by ring closure of o-4′-*ethyl*-1′-*naphthylbenzoic acid*.

This establishes the validity of the mechanism advanced by Bally and Scholl for the formation of *meso*benzanthrone by the interaction of glycerol, anthranol, and concentrated sulphuric acid. Meerwein's mechanism would require the formation of 3′-ethyl*meso*benzanthrone.

*meso*BENZANTHRONE was first synthesised by Bally (*Ber.*, 1905, **38**, 194) by the action of glycerol and sulphuric acid on anthraquinone. Bally and Scholl (*Ber.*, 1911, **44**, 1656) maintained that the mechanism of the reaction was the reduction of anthraquinone to anthrone, which then condensed with acraldehyde, generated from the glycerol by the action of sulphuric acid, to yield the aldol condensation product (I). This then lost water to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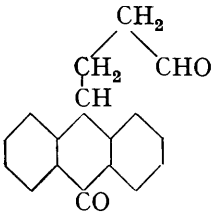
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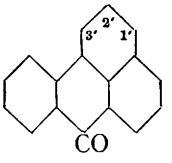
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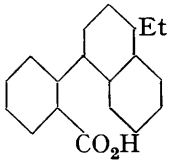
(IV.)

give the allylidene-anthrone, which cyclised to *meso*benzanthrone (III) with the loss of hydrogen, which was taken up in the reduction of more anthraquinone. This cyclisation is similar to that which acraldehyde-aniline undergoes on dry distillation (Koenigs, *Ber.*, 1880, **13**, 911); but there are difficulties in explaining this under the conditions of the experiment unless it is assumed that the cyclisation is due to the isomerisation of the unsaturated compound (I), as has been postulated by Darzens and his co-workers (*Compt. rend.*, 1926, **183**, 748, etc.) in the general synthesis of naphthalene derivatives.

Meerwein (*J. pr. Chem.*, 1918, **97**, 284) showed that anthrone can add benzylidenemalonic ester to give β-anthronyl-β-phenyl*iso*succinic ester; and he suggested that acraldehyde reacted additively with anthrone to produce β-anthronylpropaldehyde (II), which passed through 2′ : 3′-dihydro*meso*benzanthrone to *meso*benzanthrone—a cyclisation and dehydrogenation similar to that known to take place in the Skraup reaction (Blaise and Maire, *Bull. Soc. chim.*, 1908, **3**, 671).

The dehydration of α-ethylglycerol can occur in two ways to give either β-ethylacraldehyde or vinyl ethyl ketone. Catalytic dehydration gives the ketone and no aldehyde (Delaby, *Compt. rend.*, 1923, **117**, 690); but when α-ethylglycerol replaces glycerol in the Skraup reaction, a mixture of 2- and 4-ethylquinoline is produced, in which the former predominates and is even the essential constituent (Delaby and Hiron, *Compt. rend.*, 1930, **191**, 845). Since no practical details are given, we have repeated this experiment, following the conditions stated for 3-phenylquinoline (Warren, J., 1936, 1367), and have only been able to isolate 2-ethylquinoline. This fact shows directly the intermediate formation of β-ethylacraldehyde (Blaise and Maire, *loc. cit.*), the establishment of which gives a method of deciding between the two theories.

The condensation of α-ethylglycerol with anthranol in the presence of sulphuric acid results in the formation of a product which is identical with that derived from the ring closure of o-4′-*ethyl*-1′-*naphthylbenzoic acid* (IV) and therefore is 1′-*ethyl*meso*benzanthrone*, which is the product expected on the theory of Bally and Scholl (*loc. cit.*). Meerwein's mechanism (*loc. cit.*) would require the isolation of 3′-ethyl*meso*benzanthrone.

Synthesis of 1′-*Ethyl*meso*benzanthrone.*—1-Ethylnaphthalene was nitrated with fuming nitric acid at — 5° to give 4-*nitro*-1-*ethylnaphthalene*, which was reduced with stannous chloride to 4-ethyl-1-naphthylamine (compare Lesser and Glaser, *Annalen*, 1913, **402**, 11), which was transformed into 4-*iodo*-1-*ethylnaphthalene*. This was condensed with methyl *o*-iodobenzoate by the Ullmann reaction (*Annalen*, 1904, **332**, 38) to give methyl *o*-4′-ethyl-1′-naphthylbenzoate. The temperature at which this condensation was effected had a profound influence on the yield: at 280° with equimolecular proportions of the two iodo-compounds the yield was only 1% of the pure acid; but at 180° with one mole of the naphthalene and two moles of the ester the yield rose to 10% (compare Rule and Smith, J., 1937, 1096). Under the latter conditions iodobenzoic ester did not condense with 1-iodonaphthalene and the temperature had to be raised to 280° for the optimum yield. Ring closure of *o*-4′-ethyl-1′-naphthylbenzoic acid by the Friedel–Crafts reaction with the acid chloride gave 1′-ethyl*meso*benzanthrone and 2′-*ethyl*-3 : 4-*benzfluorenone* in

the proportion of about 1 to 2 respectively, but cyclisation by warming the acid with concentrated sulphuric acid resulted mainly in the fluorenone. Similar results were obtained with *o*-1′-naphthylbenzoic acid, although Schaarschmidt and Georgeacopol (*Ber.*, 1918, **51**, 1086) report only the formation of *meso*benzanthrone by the Friedel–Crafts reaction.

Experimental.

Bally's Reaction with α-Ethylglycerol.—Sulphuric acid (132 c.c.; 2·4 mols.) was stirred at room temperature while anthraquinone (9 g.; 0·043 mol.) was slowly added; when all had dissolved, water (5 c.c.) was added. The reactants were maintained at 38—42° while freshly precipitated copper (6 g.; 0·01 mol.) was added during 90 minutes; after 3 hours the copper had dissolved, the mixture acquired a yellow-brown colour, and some anthranol separated. A mixture of α-ethylglycerol (14·4 g.; 0·12 mol.) and water (14 c.c.) was added during 50 minutes while the temperature was raised to 80°; the whole was then maintained at 100° for 2½ hours. The progress of the reaction was shown by the development of a red colour; and considerable care was exercised in heating to avoid charring, which occurred only too readily. The whole was cooled and poured into boiling water (500 c.c.), boiled for a few minutes, and kept overnight. The precipitate was collected, washed with water, and boiled for 40 minutes with 1% sodium hydroxide solution (150 c.c.) to dissolve unchanged anthranol. The solution, which could not be filtered, was shaken several times with benzene, and the emulsion centrifuged into two layers. The combined benzene extracts were boiled for 2 hours with animal charcoal and filtered, and the solvent removed principally by distillation and finally by evaporation in a vacuum at the ordinary temperature. The crystals that separated were pressed on a porous plate to remove oily material and recrystallised from methyl alcohol, from which 1′-*ethyl*meso*benzanthrone* separated in yellow needles (0·5 g.), m. p. 106°, showing no depression when mixed with the specimen obtained by ring closure as below (Found : C, 88·3; H, 5·5. $C_{19}H_{14}O$ requires C, 88·3; H, 5·5%).

4-*Nitro*-1-*ethylnaphthalene.*—To 1-ethylnaphthalene (95 g.; 1 mol.) in glacial acetic acid (137 c.c.) at − 5°, 99% nitric acid (51 g.; 1·3 mols.) was added very slowly with stirring. The mixture was kept at 0° for 4 days, ice added, the precipitated oil extracted with benzene, and the extract washed with water and sodium carbonate solution. The product which distilled at 160—170°/3 mm. was redistilled. 4-*Nitro*-1-*ethylnaphthalene* was obtained as a yellow mobile liquid, b. p. 164—165°/3 mm., $d_4^{25°}$ 1·190. Yield 60 g., *i.e.*, 49% of the theoretical (Found : C, 72·0; H, 5·4; N, 6·7. $C_{12}H_{11}O_2N$ requires C, 71·6; H, 5·5; N, 7·0%).

4-*Ethyl*-1-*naphthylamine.*—A well-stirred solution of stannous chloride (187 g.; 3·1 mols.) in concentrated hydrochloric acid (80 g.; 3·3 mols.) was heated on a water-bath and 4-nitro-1-ethylnaphthalene (30 g.; 0·5 mol.), dissolved in hot alcohol (30 c.c.), was added during 1 hour. Pure nitro-compound (30 g.) was then added more rapidly, and heating continued for another hour. The whole was steam-distilled to remove unreduced nitro-compounds, made alkaline, steam passed to effect the separation of the base from the solid, and the solution extracted with ether. 4-Ethyl-1-naphthylamine was isolated as a dark-coloured oil, readily oxidised in the air, b. p. 170°/8 mm. Yield 35 g., *i.e.*, 69% of the theoretical. 4-*Ethylaceto*-1-*naphthalide* separated from methyl alcohol in colourless needles, m. p. 151° (Found : C, 78·6; H, 7·1; N, 6·7. $C_{14}H_{15}ON$ requires C, 78·8; H, 7·1; N, 6·6%).

4-*Iodo*-1-*ethylnaphthalene.*—The amine (38 g.; 1 mol.), dissolved in hot 2N-sulphuric acid (440 c.c.; 2 mols.), was cooled quickly to 0° and diazotised with sodium nitrite (14·3 g.; 0·93 mol.) in water (30 c.c.). Potassium iodide (44 g.; 1·2 mols.), dissolved in water, was added at 0° and the solution was stirred for 2 hours, heated to 100°, cooled, and treated with sodium bisulphite. The separated oil, extracted with benzene, was distilled to give 4-*iodo*-1-*ethylnaphthalene* as a light yellow oil, b. p. 170°/7 mm., readily decomposed on heating at the ordinary pressure, especially in the presence of moisture. Yield 30 g., *i.e.*, 48% of the theoretical (Found : I, 45·4. $C_{12}H_{11}I$ requires I, 45·0%).

o-4′-*Ethyl*-1′-*naphthylbenzoic Acid.*—A mixture of 4-iodo-1-ethylnaphthalene (5 g.; 1 mol.) and methyl *o*-iodobenzoate (10 g.; 2·1 mols.) in a dry tube fitted with a mercury-sealed stirrer was heated to 180°, copper-bronze added during 45 minutes, and heating continued for 4 hours. The oil was extracted with acetone and hydrolysed with alcoholic potassium hydroxide, the alcohol evaporated, and the product taken up in water. After extraction with benzene to remove neutral compounds and boiling with animal charcoal, the solution was acidified and extracted with ether. The sticky solid from the ethereal extract was lixiviated with benzene and filtered from diphenic acid. The benzene extract gave an oil, which was esterified and distilled. The

distillate, b. p. about 200°/1 mm., gave on hydrolysis o-4′-*ethyl*-1′-*naphthylbenzoic acid*, which crystallised from methyl alcohol in long colourless cubes, m. p. 176°. Yield 0·5 g., equivalent to 10% of the theoretical calculated on the iodoethylnaphthalene (Found: C, 82·5; H, 5·7. $C_{19}H_{16}O_2$ requires C, 82·6; H, 5·8%).

1′-*Ethyl*meso*benzanthrone*.—(a) *Friedel–Crafts reaction* (compare Schaarschmidt and Georgeacopol, *loc. cit.*). The above acid (0·15 g.) gave a neutral product (0·13 g.), which crystallised from methyl alcohol to give a mixture of yellow and orange-red crystals; these were separated mechanically. The yellow material, recrystallised from methyl alcohol, gave 1′-ethyl*meso*benzanthrone in yellow needles (0·03 g.), m. p. 106°, slightly soluble in alcohol with an orange-green fluorescence, and giving a deep red colour with concentrated sulphuric acid (Found: C, 88·2; H, 5·4. Calc. for $C_{19}H_{14}O$: C, 88·3; H, 5·5%). The orange-red crystals were recrystallised from acetic acid to give 2′-*ethyl*-3 : 4-*benzfluorenone* (0·06 g.), m. p. 139°, which gave a green colour with concentrated sulphuric acid (Found: C, 87·9; H, 5·5. $C_{19}H_{14}O$ requires C, 88·3; H, 5·5%).

(b) The above acid (0·15 g.) was heated with 90% sulphuric acid (10 c.c.) at 50° for 2 hours, and the solid precipitated with water was warmed with sodium carbonate solution, washed, and fractionally crystallised as above. The yield was 0·005 g. of 1′-ethyl*meso*benzanthrone and 0·1 g. of 2′-ethyl-3 : 4-benzfluorenone.

o-1′-*Naphthylbenzoic Acid*.—1-Iodonaphthalene (5 g.; 1 mol.) and methyl *o*-iodobenzoate (10 g.; 1·94 mols.) were condensed in the presence of copper-bronze (15 g.; 12 mols.) at 280° as above. The benzene solution, filtered from the diphenic acid, gave a semi-solid, which on crystallisation from methyl alcohol gave *o*-1′-naphthylbenzoic acid, m. p. 161° (Schaarschmidt and Georgeacopol, *loc. cit.*, give 161°), the yield being 30% of the theoretical calculated on the iodonaphthalene. Ring-closure of the acid by the two methods described above gave a mixture of *meso*benzanthrone and benzfluorenone in corresponding yields.

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