22. *Syntheses in the Naphthalene Series. Part III.* 1-*Hydroxy*-2 : 3-*benzfluorene and* 4-*Hydroxy*-2-*methyl*-5 : 6-*benzcoumaran.*

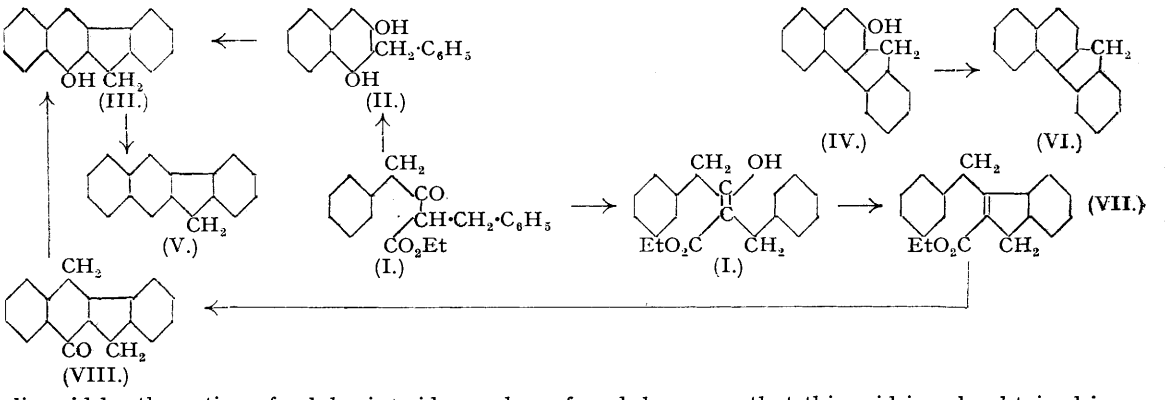
By Albert Latif and Gabra Soliman.

Ethyl α-benzyl-γ-phenylacetoacetate was prepared by the action of benzyl chloride on the sodio-derivative of ethyl γ-phenylacetoacetate and converted into 1-*hydroxy*-2 : 3-*benzfluorene* by the action of cold sulphuric acid. Analogously *ethyl γ-phenyl-α-allylacetoacetate* was prepared and converted into 4-*hydroxy*-2-*methyl*-5 : 6-*benzcoumaran.*

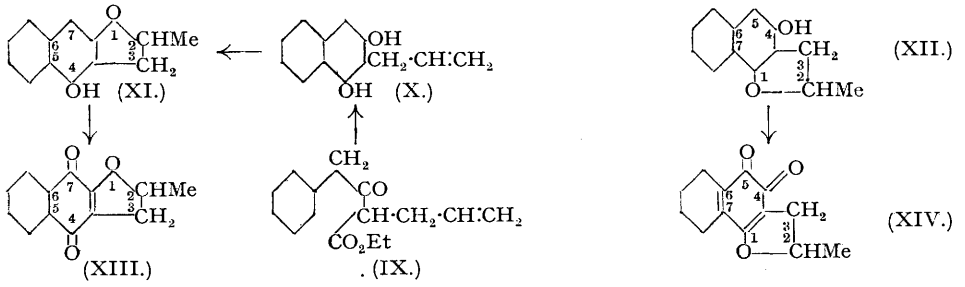
Ethyl α-benzyl- and *α-allyl-γ-phenylacetoacetate* (I and IX), prepared by the action of benzyl chloride and allyl iodide respectively on ethyl sodio-γ-phenylacetoacetate in absolute alcohol, were cyclised by cold sulphuric acid (cf. Soliman and West, this vol., p. 53).

The ester (I) gave a product, $C_{17}H_{12}O$, which formed a monoacetate and a methyl ether and could be either 1-*hydroxy*-2 : 3-*benzfluorene* (III) or 1-hydroxy-3 : 4-benzfluorene (IV). Its identity with the former was proved by distillation with zinc dust, whereby 2 : 3-benzfluorene (V) (Thiele and Wanscheidt, *Annalen*, **1910**, **376**, **269**; Koelsch, *J. Amer. Chem. Soc.*, **1933**, **55**, 3885) was obtained, identical with a specimen prepared by condensation of *o*-phthalaldehyde with α-hydrindone and distillation of the resulting benzfluorenone with zinc dust (cf. Thiele and Wanscheidt, *loc. cit.*).

Ethyl 3-benzylindene-2-carboxylate (VII) is another possible intermediate cyclisation product of the ester (I), since Roser (*Annalen*, 1888, **247**, 157) converted ethyl α-benzylacetoacetate into 3-methylindene-2-carb-



oxylic acid by the action of sulphuric acid; we have found, however, that this acid is only obtained in poor yield and therefore its formation does not represent the main reaction.



The cyclisation product of the ester (IX) had the formula $C_{13}H_{12}O_2$ and formed a *monoacetate*. It was shown to be 4-*hydroxy*-2-*methyl*-5 : 6-*benzcoumaran* (XI) by oxidation with chromium trioxide in acetic acid to 2-methyl-5 : 6-benzcoumaran-4 : 7-quinone (XIII), identical with a specimen prepared by Fieser's method (*J. Amer. Chem. Soc.*, 1926, **48**, 3206; his name for the compound is 1-methyl-4 : 5-benz-3 : 6-coumaran-quinone) The failure to isolate the *o*-quinone (XIV) by extraction of the oxidation product with saturated sodium bisulphite solution excludes the presence of the isomeric compound (XII).

Experimental.

Ethyl α-Benzyl-γ-phenylacetoacetate.—Benzyl chloride (1 mol.; 21 g.) was heated with the sodio-derivative (1 mol.) of ethyl γ-phenylacetoacetate (30·9 g.) in absolute alcohol for 5 hours, the alcohol distilled, and the *ester* extracted with ether, washed, dried, recovered as a yellowish viscous oil, and distilled, giving a fraction (31 g.), b. p. 170—175°/5 mm., 182—184°/7 mm. after redistillation; it gave a violet colour with ferric chloride (Found: C, 77·1; H, 6·5. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8%).

1-*Hydroxy*-2 : 3-*benzfluorene.*—The preceding ester (10 g.) was gradually added to ice-cold sulphuric acid (30 c.c.) and the solution was kept at room temperature for 24 hours and then stirred into warm water. The crystalline precipitate obtained, m. p. 162°, separated from benzene–light petroleum in whitish needles (4 g.), m. p. 164° (Found: C, 87·7; H, 5·0. $C_{17}H_{12}O$ requires C, 87·9; H, 5·2%). It formed in concentrated sulphuric acid a yellow solution having a blue fluorescence, and its colourless solution in aqueous sodium hydroxide exhibited a blue fluorescence. The comparatively low yield (52%) of the product appeared to be due to sulphonation, since much reddish water-soluble barium salt was isolated when the acid mother-liquor was neutralised with barium carbonate. The use of warm water for precipitation greatly enhanced the agglomeration of the product, thus facilitating its isolation by filtration. Otherwise, the product was obtained in a finely divided form, and, when ether was used for its isolation, it was contaminated with impurities.

Acetate. The hydroxy-compound (0·5 g.) was heated with acetic anhydride (5 c.c.) and pyridine (5 c.c.) for an hour. The *acetate*, isolated in the usual manner, crystallised from alcohol in needles, m. p. 171° (Found: C, 83·1; H, 5·0. $C_{19}H_{14}O_2$ requires C, 83·2; H, 5·1%).

Methyl ether. The fluorenol (2 g.), dissolved in 5% sodium hydroxide solution (60 c.c.), was shaken with methyl sulphate (6 c.c.) with cooling. The *methyl* ether crystallised from methanol in whitish plates, m. p. 70°. It gave in sulphuric acid a yellow solution having a greenish fluorescence (Found: C, 87·7; H, 5·9. $C_{18}H_{14}O$ requires C, 87·8; H, 5·7%).

2 : 3-*Benzfluorene.* When the fluorenol (1 g.) was distilled with zinc dust, a pinkish-white solid distillate (0·3 g.) was obtained, which crystallised from benzene–absolute alcohol in white plates, m. p. 209°, not depressed by an authentic specimen (Found: C, 94·1; H, 5·8. Calc. for $C_{17}H_{12}$: C, 94·4; H, 5·6%).

Synthesis of 2 : 3-*Benzfluorene.*—A solution of *o*-phthalaldehyde (5 g.) and α-hydrindone (5 g.) in methanol (50 c.c.) was refluxed for 30 minutes, a 28% solution of methyl-alcoholic potash (13 c.c.) then added dropwise, and heating continued for another hour. After cooling, 2 : 3-benzfluorenone (8 g.) separated; it crystallised from alcohol in yellow needles m. p. 152°. Distillation of the ketone with zinc dust gave the hydrocarbon in good yield. It crystallised from benzene absolute alcohol in plates, m. p. 209°.

3-*Methylindene*-2-*carboxylic Acid.*—Ethyl α-benzylacetoacetate was treated with cold sulphuric acid, and the solution kept at room temperature for 24 hours. The acid, obtained in very poor yield, crystallised from alcohol in needles m. p. 199—200°.

Ethyl γ-Phenyl-α-allylacetoacetate.—This was prepared (allyl iodide, 28 g.) in the same way as the α-benzyl ester. Distillation of the *ester* gave a fraction (23 g.), b. p. 160—162°/6 mm., which gave a violet-red colour with ferric chloride (Found: C, 73·0; H, 7·1. $C_{15}H_{18}O_3$ requires C, 73·2; H, 7·3%).

4-Hydroxy-2-methyl-5 : 6-benzcoumaran.—A solution of the preceding ester (8 g.) in ice-cold sulphuric acid (25 c.c.) was kept at room temperature for 24 hours and then poured on ice. The gummy product that separated solidified (4 g.) at room temperature after some time. It formed whitish prisms, m. p. 128°, from light petroleum but was better crystallised from dilute acetic acid. After sublimation in a high vacuum and two crystallisations from methanol it formed whitish plates, m. p. 130°, which gave a violet-red colour with ferric chloride and a pinkish colour with aqueous sodium hydroxide (Found: C, 78·1; H, 6·0. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0%). The *monoacetate* (pyridine–acetic anhydride method) crystallised from dilute methanol in white plates, m. p. 93° ((Found: C, 74·3; H, 5·8. $C_{15}H_{14}O_3$ requires C, 74·3; H, 5·8%).

2-Methyl-5 : 6-benzcoumaran-4 : 7-quinone.—A solution of the foregoing compound (1·1 g.) in acetic acid (15 c.c) was gradually treated with a solution of chromium trioxide (0·8 g.) in acetic acid (10 c.c.) and water (0·5 c.c.), and the mixture kept at room temperature for an hour and then extracted with ether after dilution with water. The ethereal solution, after being extracted with sodium bicarbonate and sodium bisulphite solutions, was evaporated. Extraction of the orange-yellow resinous residue with light petroleum gave a yellow crystalline product (0·4 g.), m. p. 164°, which, recrystallised from benzene–light petroleum, formed needles, m. p. 167°, not depressed by an authentic specimen (Found: C, 72·9; H, 4·6. Calc. for $C_{13}H_{10}O_3$: C, 72·9; H, 4·7%) prepared by Fieser's method (*loc. cit.*), which also yielded 2-methyl-6 : 7-benzcoumaran-4 : 5-quinone (XIV), m. p. 133°.

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