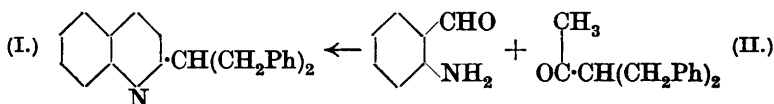


CCCXXXVIII.—*Dibenzylquinaldine*.

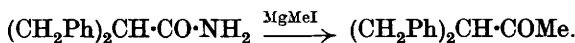
By WILLIAM HOBSON MILLS and ARNOLD THOMAS AKERS.

As described in the foregoing paper, the action of benzyl iodide on the methylene base obtained by the action of alkalis on quinaldine ethiodide resulted in the production of a compound, which from its composition and method of formation was regarded as the ethiodide of dibenzylquinaldine (I).



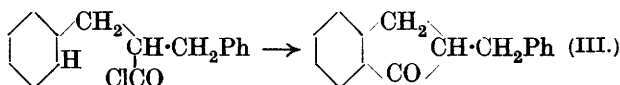
To confirm that view of its constitution the synthesis of this previously unknown base was undertaken from *o*-aminobenzaldehyde and dibenzylacetone (II), according to the general method of

Friedländer for the synthesis of bases of the quinoline series (*Ber.*, 1882, **15**, 2574). Dibenzylacetone, which also has not been previously described, could not be obtained by the ketone fission of dibenzylacetoacetic ester, hydrolysis of which under various conditions gave only dibenzylacetic acid. It was, however, readily prepared by treating the amide of dibenzylacetic acid (Schneidewind, *Ber.*, 1888, **21**, 1328) with a large excess of magnesium methyl iodide :

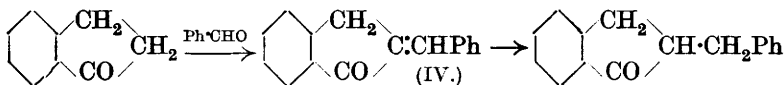


Both this reaction and the Friedländer synthesis proceeded smoothly and the ethiodide of the resulting dibenzylquinaldine proved to be identical with the compound obtained by the action of benzyl iodide on the methylene base. The interpretation of the course of this interaction explained in the foregoing paper was thus established.

In preparing dibenzylacetyl chloride for the purpose of obtaining the corresponding amide the observation was made that this acid chloride lost hydrogen chloride with remarkable ease when heated, forming a compound which was evidently benzylhydrindone (III), since it had ketonic properties, forming a *semicarbazone*.



A proof of its constitution was obtained by showing that it was also formed by reduction of benzylidenhydrindone (IV) (Kipping, *J.*, 1894, **65**, 498), a method of formation which leaves no doubt as to its structure.



We subsequently found that the facility with which dibenzylacetyl chloride lost hydrogen chloride had already been observed by Leuchs, Wutke, and Gieseler (*Ber.*, 1913, **46**, 2200) and that they had also demonstrated the constitution of the product, although in a less simple manner.

#### EXPERIMENTAL.

*Dibenzylacetamide*.—When a solution of acetoacetic ester in absolute alcohol was treated with sodium ethoxide (1 mol.) and benzyl chloride (1 mol.) and the mixture after completion of the reaction was treated again in the usual way with the same reagents (1 mol. of each), the principal product was not dibenzylacetoacetic

ester \* but dibenzylacetic ester, b. p.  $209^{\circ}/19$  mm. (Found : C, 80.5; H, 7.4. Calc., C, 80.6; H, 7.5%). The ester was readily hydrolysed by hot dilute alcoholic potash to dibenzylacetic acid, and we found this a more convenient method of preparing the acid than the hydrolysis of dibenzylmalonic ester (Bischoff and Siebert, *Annalen*, 1887, 239, 92).

To obtain the acid chloride (compare Leuchs, Wutke, and Gieseler, *loc. cit.*) the acid was heated on the water-bath for 4 hours with a slight excess of thionyl chloride. The product was then distilled rapidly under diminished pressure, when a nearly colourless oil, b. p.  $197^{\circ}/12$  mm., was obtained (Found : Cl, 13.5. Calc., Cl, 13.7%). The acid amide (compare Schneidewind, *loc. cit.*) was obtained by pouring the crude acid chloride, without removal of the slight excess of thionyl chloride, into a large excess of ammonia ( $d$  0.88) at  $0-5^{\circ}$ . The precipitated amide after crystallisation from benzene had m. p.  $128-129^{\circ}$  (Found : C, 80.1; H, 7.1; N, 5.8. Calc., C, 80.3; H, 7.2; N, 5.9%). In this manner 30 g. of recrystallised amide were obtained from 40 g. of acid.

as-Dibenzylacetone,  $(C_6H_5 \cdot CH_2)_2CH \cdot CO \cdot CH_3$ .—To a solution of magnesium (14.8 g.) in methyl iodide (40 c.c.) and anhydrous ether was added solid dibenzylacetamide, and the mixture was boiled for 18 hours. After decomposition of the magnesium compound with ice and dilute sulphuric acid the ethereal layer was separated. On evaporation of the ether the ketone was left as an oil, b. p.  $120-122^{\circ}/16$  mm. (Found : C, 85.5; H, 7.65.  $C_{17}H_{18}O$  requires C, 85.7; H, 7.6%). Yield 21 grams.

Benzylidenedibenzylacetone,  $(C_6H_5 \cdot CH_2)_2CH \cdot CO \cdot CH : CH \cdot C_6H_5$ .—To an alcoholic solution (150 c.c.) of dibenzylacetone (3 g.) and benzaldehyde (1.3 g.), 10% aqueous sodium hydroxide (3 c.c.) was added, and the mixture left for 3 days. The crystalline precipitate formed was recrystallised from alcohol; m. p.  $66-67^{\circ}$  (Found : C, 88.6; H, 6.7.  $C_{24}H_{22}O$  requires C, 88.4; H, 6.75%).

Dibenzylquinaldine (I).—To an alcoholic solution of *o*-amino-benzaldehyde (1 part) and dibenzylacetone (2 parts) a little solid potassium hydroxide was added and the mixture was boiled for 5 hours. Water was then added and the alcohol evaporated, when the product was deposited as a pasty mass which, after keeping for some days in a desiccator, partly crystallised. The crystals, separated and recrystallised from methyl alcohol, gave colourless needles, m. p.  $74^{\circ}$  (Found : C, 89.4; H, 6.5; N, 4.4.  $C_{24}H_{21}N$  requires C, 89.2; H, 6.5; N, 4.3%). Yield 50%.

Dibenzylquinaldine Methiodide.—Dibenzylquinaldine was heated

\* This was obtained by Fittig and Christ (*Annalen*, 1892, 268, 124) by treating acetoacetic ester with 1 or  $1\frac{1}{2}$  mols. of sodium ethoxide and benzyl chloride.

with excess of methyl iodide for 24 hours at 100°. The crystalline deposit formed separated from methyl alcohol in yellow prisms, m. p. 204° (Found : I, 27.5.  $C_{25}H_{24}NI$  requires I, 27.3%).

*Dibenzylquinaldine ethiodide* was prepared similarly to the methiodide except that the heating was continued for 48 hours. Yellow prisms, m. p. 215—216° (Found : C, 64.9; H, 5.5; I, 26.7. Calc., C, 65.1; H, 5.4; I, 26.5%). The compound was identical with that obtained by the action of benzyl iodide on 1-ethyl-2-methylene-1 : 2-dihydroquinoline.

*2-Benzyl-1-hydrindone*.—Similarly to Leuchs, Wutke, and Gieseler (*loc. cit.*), we found that if in the preparation of dibenzylacetyl chloride, phosphorus pentachloride was employed, or if when using thionyl chloride the distillation was carried out too slowly or at too high a pressure, the chief product was benzylhydrindone (Found : C, 86.5; H, 6.3. Calc., C, 86.5; H, 6.3%). The *semicarbazone*, crystallised from alcohol, had m. p. 198—199° (Found : N, 15.2.  $C_{17}H_{17}ON_3$  requires N, 15.05%).

*Reduction of Benzylidenehydrindone*.—Benzylidenehydrindone was prepared as described by Kipping (J., 1894, 65, 480) except that thionyl chloride was used instead of phosphorus pentachloride for the preparation of phenylpropionyl chloride and zinc chloride was employed instead of alcoholic potassium hydroxide for the condensation of hydrindone with benzaldehyde, equimolecular quantities of the latter two compounds being heated together for 8 hours on the water-bath with a little anhydrous zinc chloride, and the product separated by dissolving in alcohol and pouring into cold water. The reduction of benzylidenehydrindone to benzylhydrindone was carried out as follows: Benzylidenehydrindone (10 g.) was dissolved in a mixture of methyl and ethyl alcohol, and 3.3% sodium amalgam (300 g.) was added gradually during 4 hours, the mixture being kept neutral to phenolphthalein by the regulated addition of 50% acetic acid. After evaporation of the alcohol, water was added and the product was extracted with ether. It boiled at 222°/18 mm. and its identity with the compound formed by loss of hydrogen chloride from dibenzylacetyl chloride was shown by conversion into the semicarbazone (Found : C, 73.5; H, 5.6. Calc. for  $C_{17}H_{17}ON_3$ , C, 73.1; H, 6.1%). The m. p. of this semicarbazone as well as the "mixed m. p." with the semicarbazone of the ketone obtained from diphenylacetyl chloride was 198—199°.

The analyses for carbon, hydrogen and nitrogen recorded in this paper were carried out by Mr. F. H. Flack.

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