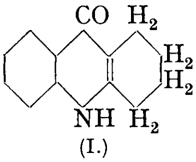
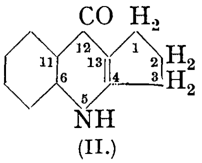
78. *The Reaction between Anthranilic Acid and* cyclo*Pentanone.*

By B. K. Blount and S. G. P. Plant.

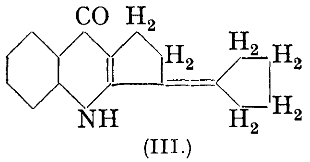
Although the reaction employed by Tiedtke (*Ber.*, 1909, **42**, 621) for the preparation of tetrahydroacridone (I) from anthranilic acid and *cyclo*hexanone has been applied to suberone and α-hydrindone, with the formation of the corresponding quinolones (Perkin and Plant, J., 1928, 2583; Blount, Perkin, and Plant, J., 1929, 1975), yet it was found impossible to obtain 12-keto-2 : 3 : 5 : 12-tetrahydro-β-quinindene (II) by an analogous method from *cyclo*pentanone (Blount, Perkin, and Plant, *loc. cit.*). Instead, the isolation of a small quantity of a substance, m. p. 272°, which appeared to have the formula $C_{17}H_{19}O_2N$, was recorded, but this compound has now been obtained in much greater yields under conditions described in the experimental section, and found to melt, when pure, at 285° and possess the molecular formula $C_{17}H_{17}ON$. It therefore seemed probable that the product had resulted from the primary conversion of the *cyclo*pentanone into *cyclo*pentylidene-*cyclo*pentanone, followed by the normal Tiedtke reaction. This view was supported by the preparation of the substance from anthranilic acid and *cyclo*pentylidene*cyclo*pentanone obtained by the method of Wallach (*Ber.*, 1896, **29**, 2955), who made the significant observation that *cyclo*pentanone undergoes intermolecular condensation much more readily than *cyclo*hexanone or suberone.



(I.)



(II.)



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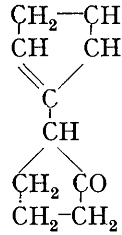
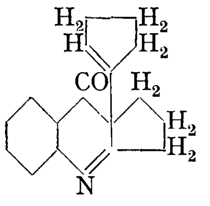
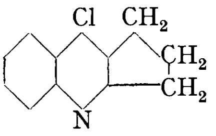


(IV.)



(V.)



(VI.)

The product must be regarded as 12-*keto*-3-cyclo*pentylidene*-2 : 3 : 5 : 12-*tetrahydro*-β-*quinindene* (III), although the possibility of *cyclo*pentylidene*cyclo*pentanone reacting in the isomeric form (IV) (Dickins, Hugh, and Kon, J., 1929, 572) admits the alternative structure (V). The latter alternative was eliminated, however, by the conversion of the substance, by means of phosphorus oxychloride, into a compound derived from the replacement of hydroxyl by a single chlorine atom. Under similar conditions (II) was converted into 12-*chloro*-2 : 3-*dihydro*-β-*quinindene* (VI), but the reaction with (V) would be more complex.

Experimental.

12-*Keto*-3-cyclo*pentylidene*-2 : 3 : 5 : 12-*tetrahydro*-β-*quinindene*.—A mixture of equal weights (10·7 g.) of anthranilic acid and *cyclo*pentanone was gradually heated to 265°, under a reflux air condenser, and maintained at this temperature for 10 minutes. The product was cooled, dissolved in a little hot alcohol, and poured into dilute ammonia to remove unchanged anthranilic acid. When the precipitated sticky solid was crystallised from alcohol, 12-*keto*-3-cyclo*pentylidene*-2 : 3 : 5 : 12-*tetrahydro*-β-*quinindene* was obtained in yellow needles (1·9 g.), which, after recrystallisation from anisole, melted at 285°, with darkening at 263° (Found : C, 81·4; H, 6·8. $C_{17}H_{17}ON$ requires C, 81·3; H, 6·8%).

The same substance (1·5 g.; no depression in a mixed m. p.; found : C, 81·3; H, 6·9%) was obtained when a mixture of anthranilic acid (4 g.) and *cyclo*pentylidene*cyclo*pentanone (4·2 g.) was heated under similar conditions, and the product treated as before. It was insoluble in hot water, but dissolved in hot dilute hydrochloric acid, from which the hydrochloride separated, on cooling, in nearly colourless needles; the salt gave the base again on treatment with cold water.

12-*Chloro*-3-cyclo*pentylidene*-2 : 3-*dihydro*-β-*quinindene*.—A solution of the above base in ten times its weight of phosphorus oxychloride was refluxed for ½ hour, cooled, and poured into ice-water. When the yellow solid which soon separated was ground with dilute ammonia, 12-*chloro*-3-cyclo*pentylidene*-2 : 3-*dihydro*-β-*quinindene* was obtained; a further quantity resulted when the aqueous solution was made alkaline. This substance separated from alcohol in almost colourless plates, m. p. 110° (Found : C, 75·5; H, 5·9; Cl, 13·1. $C_{17}H_{16}NCl$ requires C, 75·7; H, 5·9; Cl, 13·2%).

By a similar process 12-*chloro*-2 : 3-*dihydro*-β-*quinindene* was obtained from 12-keto-2 : 3 : 5 : 12-tetrahydro-β-quinindene. A clear solution resulted after the reaction mixture had been left with ice-water, but the product was isolated by making this alkaline, and purified by boiling with charcoal in alcohol. It then separated from aqueous alcohol in colourless needles, m. p. 70° (Found : Cl, 17·4. $C_{12}H_{10}NCl$ requires Cl, 17·4%).

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