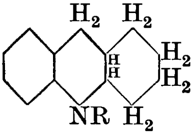
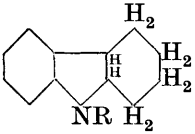
CCLVIII.—*Stereoisomerism in Polycyclic Systems. Part VI.*

By BERTIE KENNEDY BLOUNT, WILLIAM HENRY PERKIN, jun., and SYDNEY GLENN PRESTON PLANT.

IN the earlier communications in this series (J., 1924, **125**, 2437; 1926, 438; 1927, 2676; 1928, 639, 2583), the possibilities of preparing two stereoisomeric modifications of octahydroacridine (I; R = H), hexahydrocarbazole (II; R = H), 2 : 3 : 4 : 5 : 12 : 13-

hexahydro-β-quinindene * (III; $R = H$), 2 : 3 : 4 : 5 : 11 : 12-hexahydroheptindole (IV; $R = H$), and 5 : 7 : 8 : 9 : 10 : 11 : 14 : 15-octahydroheptaquinoline (V; $R = H$) have been studied. The existence of stereoisomerides in some of these cases is due to the


(I.)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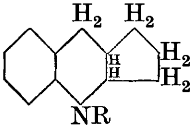
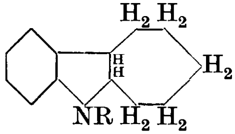
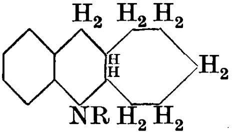

(III.)

(IV.)



(V.)

cis- and *trans-*unions of two ring systems, and the relative proportions of the stereoisomerides formed in any given instance during the reduction of the appropriate parent substance have been shown to be in accordance with deductions which can be drawn concerning the relative strain in the various configurations. It has been pointed out in these communications, however, that several factors must take part in determining the relative proportions of the two stereoisomerides in any given case, and, in order to obtain further light on some of the problems previously discussed, the investigations have now been extended to the reduction of other compounds closely related to those already studied.

A surprising feature of the earlier work is the fact that the reduction of tetrahydroacridone (VI) with sodium amalgam yields only one of the two modifications of octahydroacridine, whereas considerable quantities of both forms of the latter substance are readily produced by the reduction of tetrahydroacridine with tin and aqueous-alcoholic hydrochloric acid. It has also been observed that the reduction of 11-keto-5 : 7 : 8 : 9 : 10 : 11-hexahydroheptaquinoline (VII) leads to only one of the two possible forms of (V;

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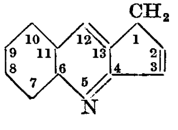
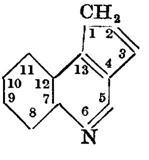
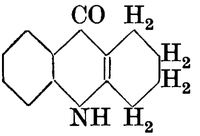
* In the previous communications this compound has been called "2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene," but the preparation of certain substances described in the present paper necessitated a small alteration in the nomenclature employed. The hypothetical parent substance (IIIA) is now called "β-quinindene," and the isomeric substance (IIIB) is called "α-quinindene."

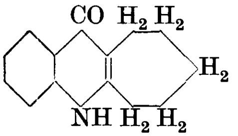
(IIIA.)



(IIIB.)

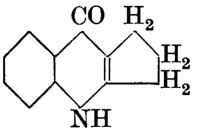
R = H). On account of the ease with which both modifications of (III; R = H) are obtained by reducing 2 : 3-dihydro-β-quinindene, it was considered of interest to investigate the action of sodium amalgam on 12-*keto*-2 : 3 : 5 : 12-*tetrahydro*-β-*quinindene* (VIII).



(VI.)

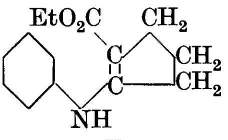


(VII.)

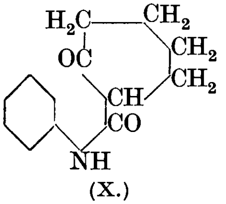


(VIII.)

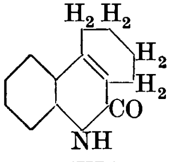
The preparation of this substance presented unexpected difficulties. Tetrahydroacridone is formed easily by condensing anthranilic acid with *cyclo*hexanone (Tiedtke, *Ber.*, 1909, **42**, 624), and, since this reaction can be applied without difficulty to the preparation of (VII) by the use of suberone, it was thought that the interaction of anthranilic acid and *cyclo*pentanone would yield (VIII). This has not been accomplished, but there has been isolated from the reaction mixture a small quantity of a *substance* which melts at 272° and appears to have the formula $C_{17}H_{19}O_2N$, but its nature has not yet been established. It was found, however, that aniline and ethyl *cyclo*pentanone-2-carboxylate reacted slowly at room temperature to give ethyl 1-anilino-$\Delta^{1:2}$-*cyclo*pentene-2-carboxylate (IX), and that this, on being heated for a short time at 260°, yielded the required substance (VIII). In order to confirm the view that under these conditions the reaction between aniline and ethyl *cyclo*pentanone-2-carboxylate takes the course indicated, which is in accordance with general experience during the preparation of quinoline derivatives from β-ketonic esters, the interaction of aniline and ethyl *cyclo*hexanone-2-carboxylate under similar conditions was investigated. It was found that *ethyl* 1-*anilino*-$\Delta^{1:2}$-cyclo*hexene*-2-*carboxylate* (m. p. 58·5°) was first formed and that this then yielded tetrahydroacridone, identical with the product prepared by Tiedtke's method. The reaction between aniline and ethyl *cyclo*hexanone-2-carboxylate has been studied by Kötz and Merkel (*J. pr. Chem.*, 1909, **79**, 122), who claim to have prepared ethyl



(IX.)



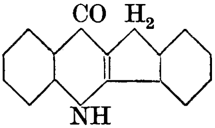
(X.)

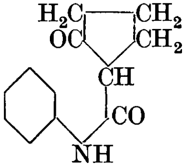


(XI.)

1-anilino-$\Delta^{1:2}$-*cyclo*hexene-2-carboxylate (the m. p. of which they state to be 29°) by heating a mixture of the two reagents and keeping the product for several days. We have now found that, by boiling a mixture of these two substances for 2 minutes, *cyclohexanone-2-carboxyanilide* (m. p. 105°) (X) is produced, and that this, on treatment with concentrated sulphuric acid on the steam-bath, passes into 9-*keto*-5 : 6 : 7 : 8 : 9 : 10-*hexahydrophenanthridine* (XI). It appears possible, therefore, that the product of Kötz and Merkel was not a single substance. The failure of Tiedtke's reaction in the case of *cyclo*pentanone was surprising, and, in order to discover whether this is characteristic of cyclic ketones with a 5-membered ring, the reaction was applied to α-hydrindone, but it then proceeded normally with the production of 14-*keto*-7 : 14-*dihydrobenzo*-β-*quinindene* (XII).

(XII.)

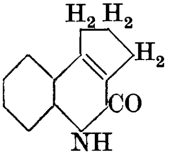




(XIII.)

The reduction of (VIII) in alcoholic solution with sodium amalgam yielded an oily, basic product, from which, after benzoylation, both 5-benzoyl-2 : 3 : 4 : 5 : 12 : 13-hexahydro-β-quinindene (A) and (B) were isolated. The two products were identical in every way with the two modifications (m. p.'s 174° and 161°) described in Part IV of this series. It was found, however, that the (B) modification greatly preponderated in the reaction mixture, and it is estimated that the ratio of the amounts of the (A) and (B) forms present is approximately 1 : 15, whereas the ratio in the product of the reduction of 2 : 3-dihydro-β-quinindene was 1 : 3. Thus, whilst the reduction of this keto-compound (VIII) does actually give both stereoisomerides, the product consists very largely of that modification which is most readily produced by the alternative method. This fact is interesting, because the single modification (A) of octahydroacridine which is obtained from tetrahydroacridone is the one which is formed to far the smaller extent during the reduction of tetrahydroacridine (Part V). Since it was thought that the latter observation might possibly be explained by the conversion of octahydroacridine (B) into its stereoisomeride under the conditions used for reducing tetrahydroacridone, octahydroacridine (B) was submitted to the action of sodium amalgam in boiling alcohol, but was recovered completely unchanged.

The results so far obtained indicated that it would be interesting to extend these investigations to related compounds in the α-quinindene series, in which the *cyclo*pentane ring is attached to the 3 : 4- in place of the 2 : 3-position in the quinoline nucleus. For this purpose cyclo*pentanone-2-carboxyanilide* (XIII), obtained by boiling a mixture of aniline and ethyl *cyclo*pentanone-2-carboxylate for 2 minutes, was converted by the action of concentrated sulphuric acid into 5-*keto*-2 : 3 : 5 : 6-*tetrahydro-α-quinindene* (XIV). On treating this compound with sodium amalgam in boiling alcohol under the conditions previously used, it was found that the process of reduction resulted only in hydrogenation of the double bond in the 4 : 13-position, and that the reaction did not in this case lead to the fully reduced tetrahydroquinoline derivative. It is possible, however, for the resulting 5-*keto*-2 : 3 : 4 : 5 : 6 : 13-*hexahydro-α-quinindene* (XV) to appear in two stereoisomeric modifications through the *cis*- and *trans*-addition of the hydrogen atoms. A careful examination of the product of the reaction has indicated quite definitely the presence of both of these stereoisomerides. In accordance with the procedure previously adopted, the higher-melting form (m. p. 210—211°) is called (A) and the lower-melting (m. p. 135·5°) (B). The reaction product has been found to consist very largely of the (B) modification, only a small quantity of the (A) being present. It was then thought that further reduction of this mixture of the two stereoisomeric forms of (XV) with sodium and boiling alcohol would lead to the two corresponding 2 : 3 : 4 : 5 : 6 : 13-hexahydro-α-quinindenes (XVI; R = H). It was found, however, that, although reduction proceeded to the desired stage, the product consisted essentially of a single base. Since this possessed a low melting point, the reaction product was benzoylated, but careful investigation indicated the presence of only one of the two possible modifications of 6-*benzoyl*-2 : 3 : 4 : 5 : 6 : 13-*hexahydro-α-quinindene*. An explanation of the interesting fact that the reduction of a mixture of both forms of (XV) has given rise to only one form of (XVI) can be found if the reduction is assumed to take the following course :



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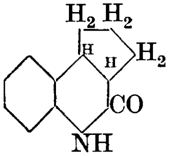
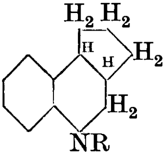
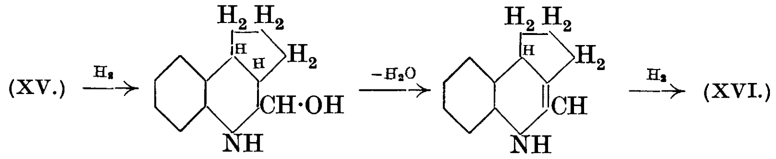


(XV.)



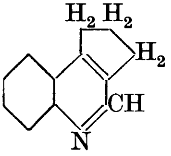
(XVI.)



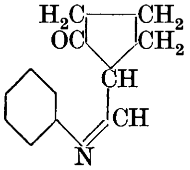
(XVII.) (XVIII.)

The formation of (XVIII) by the elimination of water from (XVII) makes it possible for a single product to result during this reduction process, but the formation of two stereoisomeric modifications of (XVI) is still theoretically possible.

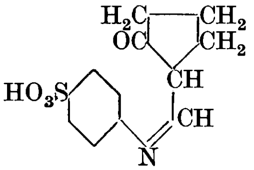
It now became of interest to study the reduction of 2 : 3-dihydro-α-quinindene (XIX), and, with this end in view, 2-phenyliminomethyl*cyclo*pentan-1-one (XX) was obtained from the condensation of aniline and 2-hydroxymethylene*cyclo*pentanone, a reaction similar to that employed by Borsche (*Annalen*, 1910, **377**, 82) for



(XIX.)



(XX.)



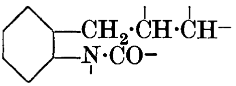
(XXI.)

the preparation of 2-phenyliminomethyl*cyclo*hexanone. Attempts to remove water from this substance with the formation of (XIX) have, however, been unsuccessful. The action of concentrated sulphuric acid, both at 100° and at 15°, led to a sulphonic acid which is probably *2-phenyliminomethyl*cyclo*pentanone-4′-sulphonic acid* (XXI), in view of the fact that Borsche obtained the corresponding sulphonic acid from the *cyclo*hexanone derivative, and established its constitution.

During the course of the present work, it became apparent that a study of the colour reactions of many of the derivatives described in this and the previous communications would be of interest and might have a direct bearing on the problem of the constitution of strychnine and brucine. The results obtained by examining the colour developed when a solution of a small quantity of the substance in 65% sulphuric acid at 0° was treated with a drop of concentrated aqueous potassium dichromate have been very instructive. The substances examined fell into three classes depending respectively upon (i) the development of an intense crimson colour which did not fade for at least one minute, (ii) the development of an intense, but rather transient, blue or violet-blue colour, or (iii) the appearance of no intense colour. For convenience the members of each class are denoted in the following table :—

(i) *Crimson colour.*	(ii) *Blue colour.*	(iii) *No intense colour.*
Both *cis*- and *trans*-modifications of 5-acetyl- and 5-benzoyl-2 : 3 : 4 : 5 : 12 : 13-hexahydro-β-quinindene (III; R = Ac or Bz).	Both *cis*- and *trans*-modifications of 9-acetyl- and 9-benzoyl-hexahydrocarbazole (II; R = Ac or Bz).	2 : 3-Dihydro-β-quinindene. 2 : 3 : 4 : 5 : 12 : 13-Hexahydro-β-quinindene (A) (III; R = H).
Both *cis*- and *trans*-modifications of 10-acetyl- and 10-benzoyl-octahydroacridine (I; R = Ac or Bz).	10-Acetyl- and 10-benzoyl-2 : 3 : 4 : 5 : 11 : 12-hexahydroheptindole (IV; R = Ac or Bz).	12-Keto-2 : 3 : 5 : 12-tetrahydro-β-quinindene (VIII). Tetrahydrocarbazole.
5-Benzoyl-5 : 7 : 8 : 9 : 10 : 11 : 14 : 15-octahydroheptaquinoline (V; R = Bz).	8-Acetyl- and 8-benzoyl-tetrahydropentindole (Plant and Rippon, J., 1928, 1906).	Both *cis*- and *trans*-hexahydrocarbazole (II; R = H).
1-Benzoyl-1 : 2 : 3 : 4-tetrahydroquinoline.	1-Benzoyl-2-methyl-2 : 3-dihydroindole (Bamberger and Sternitzki, *Ber.*, 1893, 26, 1303).	Both *cis*- and *trans*-octahydroacridine (I; R = H). Tetrahydropentindole. Tetrahydroacridone (VI). Acetanilide. Benzanilide. β-Phenylpropanilide. *N*-Ethylbenzanilide. Benzo-*o*-toluidide.

An examination of the formulæ of the members of each of these three groups brought to light a very interesting generalisation. It will be seen that all the members of group (i) contain the *N*-acyltetrahydroquinoline structure, whilst those in class (ii) contain the *N*-acyldihydroindole structure. It is, of course, possible at first sight that the colour reactions of classes (i) and (ii) may be due to the presence of the more general groupings (XXII) and (XXIII) respectively, but this can be tested, since, if it is the case, an *N*-acyltetrahydroquinoline substituted in the 3- and 4-positions (XXIV)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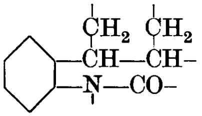
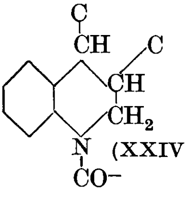
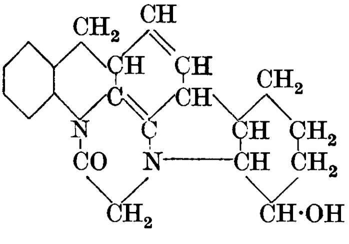

(XXIII.)


(XXIV.)

should give the colour reactions of group (ii), but, if the *N*-acyldihydroindole skeleton is the determining factor in the latter group, it should give the reaction of group (i). 6-Benzoyl-2 : 3 : 4 : 5 : 6 : 13-hexahydro-α-quinindene (XVI; R = Bz), prepared during the course of the present work, provides the means of deciding this point, and the alternative possibilities were eliminated when it was found that this substance was a typical member of group (i). Now strychnine under these conditions develops a blue colour which fades during about 30 seconds, and, in consequence, should be included in group (ii), and should contain an *N*-acyldihydroindole skeleton. Recently the original strychnine formula (XXV) of Perkin and

Robinson (J., 1910, **97**, 305) has been abandoned in favour of (XXVI) (Fawcett, Perkin, and Robinson, J., 1928, 3082; Perkin and Robinson, this vol., p. 964), and it is interesting to note that the



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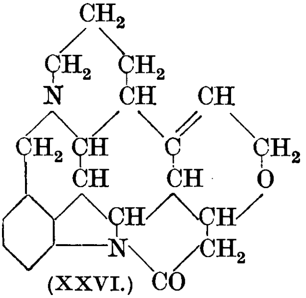

(XXVI.)

latter formula contains the *N*-acyldihydroindole structure, but that it was absent from the earlier formula.

EXPERIMENTAL.

12-*Keto*-2 : 3 : 5 : 12-*tetrahydro*-β-*quinindene*.—When a mixture of ethyl *cyclo*pentanone-2-carboxylate (52 g., prepared by the method of Dobson, Ferns, and Perkin, J., 1909, **95**, 2015) and aniline (31 g.) was kept over calcium chloride in an evacuated desiccator for a fortnight, ethyl 1-anilino-$\Delta^{1:2}$-*cyclo*pentene-2-carboxylate remained as a pale brown oil, which resisted all attempts to make it solidify. When it was heated rapidly to 260° and kept at that temperature for 5 minutes, 12-*keto*-2 : 3 : 5 : 12-*tetrahydro*-β-*quinindene* (VIII) was formed as a solid; this was purified by treatment for ½ hour with boiling benzene (500 c.c.), in which it is only very slightly soluble. After being filtered from the hot benzene, it was obtained as a colourless powder (23 g.), m. p. 325° (with previous blackening). It separated from alcohol in rectangular plates, m. p. 327° (with previous blackening) (Found : N, 7·8. $C_{12}H_{11}ON$ requires N, 7·6%). A solution of this compound (5 g.) in alcohol (300 c.c.), to which a little sodium bicarbonate had been added, was treated at its boiling point with sodium amalgam (375 g. of 4%) in portions during 6 hours, the whole being vigorously stirred and a stream of carbon dioxide being passed throughout. The resulting pasty mass was filtered, and the residue was well washed with alcohol. The united alcoholic solutions were evaporated, the product was shaken with a mixture of ether and water, and the ethereal solution was then extracted with very dilute hydrochloric acid. The bases were liberated from the acid solution by the addition of alkali, and again extracted with ether; after drying with potassium carbonate and removal of the solvent, they were obtained as a thick, dark brown oil (4 g.). After being shaken with an excess of benzoyl chloride and dilute aqueous sodium hydroxide, the product was dissolved in ether, the solution shaken with dilute hydrochloric acid, the ether removed, and the residue boiled with alcohol for ½ hour. The mixture was then steam-distilled to remove the alcohol and ethyl benzoate, after which the benzoylated product remained as a brown solid (2·5 g., m. p. 120—138°). This was purified by boiling its solution in alcohol with charcoal, filtering, and distilling off the alcohol; crystallisation from the minimum quantity of alcohol then yielded a mixture (1·55 g., m. p. 138—152°) of the two stereoisomeric 5-benzoyl-2 : 3 : 4 : 5 : 12 : 13-hexahydro-β-quinindenes (A) and (B) in a practically pure condition. When this mixture was recrystallised from acetone the (B) form (1 g., m. p. 158—159°) was obtained. Evaporation of the acetone filtrate and subsequent recrystallisation of the residue from alcohol yielded at first a further quantity of the same substance, mixed with a little of its stereoisomeride, but, after the solution had been filtered and kept for several hours, the (A) modification (0·05 g.) separated in a moderately pure condition (m. p. 159—162°) : it was obtained pure (m. p. 173°) by recrystallisation from alcohol. The identities of these two benzoyl derivatives were definitely established by determining the m. p.'s of mixtures with the products previously prepared (J., 1928, 643).

14-*Keto*-7 : 14-*dihydrobenzo*-β-*quinindene*.—A mixture of anthranilic acid (1 g.) and α-hydrindone (1 g.) was heated in an oil-bath so that the temperature gradually attained 210° during the course of ½ hour. After 15 minutes at this temperature the mixture became semi-solid, and the product was then purified by treatment with a considerable quantity of boiling benzene, in which it was insoluble. On crystallisation from *cyclo*hexanone, 14-*keto*-7 : 14-*dihydrobenzo*-β-*quinindene* was obtained in small, brown prisms, m. p. above 360° (Found : N, 5·9. $C_{16}H_{11}ON$ requires N, 6·0%).

5-*Keto*-2 : 3 : 5 : 6-*tetrahydro*-α-*quinindene* (XIV).—When a mixture of ethyl *cyclo*pentanone-2-carboxylate (13 g.) and aniline (7·75 g.) was boiled under reflux for 2 minutes, cooled, and kept for 24 hours, a solid product separated. This was collected, washed with petroleum, and then crystallised from this solvent; cyclo*pentanone*-2-*carboxyanilide* was thus obtained in colourless needles, m. p. 104° (Found : N, 6·8. $C_{12}H_{13}O_2N$ requires N, 6·9%). For the preparation of 5-*keto*-2 : 3 : 5 : 6-*tetrahydro*-α-*quinindene* the crude mixture, after heating and cooling, was added slowly, with cooling, to concentrated sulphuric acid (25 c.c.), and the whole was heated on the steam-bath for 15 minutes, and then poured into a large bulk of water; the product separated as a solid, which was subsequently obtained from 70% acetic acid in long, thin, colourless plates, m. p. 256° (Found : N, 7·6. $C_{12}H_{11}ON$ requires N, 7·6%).

The 5-*Keto*-2 : 3 : 4 : 5 : 6 : 13-*hexahydro*-α-*quinindenes*.—The foregoing compound (XIV) (5 g.) was reduced under exactly the same conditions as those described for its β-quinindene analogue. The filtered, alcoholic solution of the reduction product was evaporated almost to dryness, and benzene (150 c.c.) was added. By distilling off a portion of the benzene, traces of alcohol and water were removed, and the remaining solution was then filtered from a small quantity of suspended material. After further concentration of the benzene solution, the mixture of reduction products (3·28 g., m. p. 121—132°) separated gradually, on standing, as a colourless solid. A further quantity (0·67 g., m. p. 119—143°) was obtained from the benzene mother-liquors by concentrating them, collecting the product, and washing it with a little petroleum. By repeated crystallisation of this mixture from either benzene or alcohol, a product rich in the lower-melting stereoisomeride was obtained. By dissolving this in alcohol and allowing the solution to evaporate slowly at the ordinary temperature, 5-*keto*-2 : 3 : 4 : 5 : 6 : 13-*hexahydro*-α-*quinindene* (B) was obtained in large, thin, hexagonal plates, m. p. 135·5° (Found : C, 77·0; H, 6·9. $C_{12}H_{13}ON$ requires C, 77·0; H, 6·9%). The remaining mixture (Found, by microanalysis : C, 76·4; H, 7·0%), from which a relatively considerable amount of this stereoisomeride had been removed, and which melted at 122—174°, was crystallised from ether, whereby a very small amount of 5-*keto*-2 : 3 : 4 : 5 : 6 : 13-*hexahydro*-α-*quinindene* (A) was obtained in a pure condition as compact prisms, m. p. 210—211° (Found : C, 76·9; H, 7·0%). When the mixture was allowed to crystallise slowly from alcohol, the presence of the two types of crystal was very clearly seen.

2 : 3 : 4 : 5 : 6 : 13 - *Hexahydro* - α- *quinindene*.—The tetrahydro-compound (XIV) (10 g.) was reduced with sodium amalgam as already described, and the solvent was removed completely from the benzene solution of the mixture of the two forms of the hexahydro-compound (XV). The crude product (10 g.) was dissolved in boiling absolute alcohol (50 c.c.), and sodium (20 g.) was added gradually in small pieces, a further quantity (150 c.c.) of absolute alcohol being added in portions from time to time. The resulting mixture was acidified by addition of water (100 c.c.) and concentrated hydrochloric acid (110 c.c.), and then a considerable amount (250 c.c.) of it was removed by distillation. When the remainder was made alkaline and steam-distilled, the oily product appeared in the aqueous distillate. The residual liquid was examined, but yielded no appreciable quantity of organic material. After the

product had been extracted with ether from the steam distillate, dried over potassium carbonate, and the ether removed, the residue (7·6 g.), which solidified on cooling, was benzoylated by shaking with benzoyl chloride (7·5 g.) and an excess of dilute aqueous sodium hydroxide. The product was dissolved in ether, and the solution extracted with dilute hydrochloric acid. This aqueous extract, when made alkaline, yielded only a very small quantity of an amorphous substance, from which nothing definite could be isolated. The ethereal solution was dried and evaporated, and, after treatment of the residue with boiling alcohol, and subsequent removal of the alcohol and ethyl benzoate in steam, the product remained as a gum from which the aqueous liquid was decanted. On adding a few drops of ether, *6-benzoyl-2 : 3 : 4 : 5 : 6 : 13-hexahydro-α-quinindene* was isolated as an almost colourless solid (11·6 g., m. p. 85—95°); when recrystallised from methyl alcohol, it separated in colourless, rhombic plates, m. p. 94·5—95° (Found: C, 82·2; H, 6·8. $C_{19}H_{19}ON$ requires C, 82·3; H, 6·8%). By evaporation of the mother-liquor, further amounts of the same substance were isolated, and a careful examination of the product yielded ultimately 11·3 g. of this benzoyl derivative in a pure condition, making it quite clear that no appreciable quantity of a second stereoisomeride was present.

A mixture of 6-benzoyl-2 : 3 : 4 : 5 : 6 : 13-hexahydro-α-quinindene (5 g.), potassium hydroxide (20 g.), water (40 c.c.), and alcohol (60 c.c.) was boiled under reflux for 20 hours, the alcohol was distilled off, and the residue shaken with ether and water. The ethereal solution was extracted with dilute hydrochloric acid, the aqueous extract boiled for a few minutes, then cooled, filtered, and made alkaline by the addition of ammonia. The solid base (2·95 g.) which separated was collected after being kept at 0° over-night, and crystallised from light petroleum, from which *2 : 3 : 4 : 5 : 6 : 13-hexahydro-α-quinindene* separated in long, colourless needles, m. p. 42·5° (Found: C, 83·4; H, 9·0. $C_{12}H_{15}N$ requires C, 83·2; H, 8·7%).

After equal amounts of the base and phenylcarbimide had been warmed together for a minute at about 70°, and the product crystallised from aqueous alcohol, *6-phenylcarbamyl-2 : 3 : 4 : 5 : 6 : 13-hexahydro-α-quinindene* was obtained in long, colourless prisms, m. p. 99° (Found: N, 9·5. $C_{19}H_{20}ON_2$ requires N, 9·6%). The picrate of (XVI; R = H) separated from alcohol in yellow needles, m. p. 168°.

*2-Phenyliminomethyl*cyclo*pentanone*.—When aniline (2·5 g.), dissolved in alcohol (5 c.c.), was added to a solution of 2-hydroxymethylene*cyclo*pentanone (3 g., prepared by the method of Wallach and Steindorff, *Annalen*, 1903, **329**, 114) in alcohol (20 c.c.), the mixture became warm, and a solid began to separate. After standing for 2 hours, 2-phenyliminomethyl*cyclo*pentanone (XX) was obtained in yellow needles (3·6 g.), m. p. 174°. A mixture of this compound (1 g.) and concentrated sulphuric acid (3 c.c.) was heated on the steam-bath for 2 hours and then poured into water (50 c.c.). After 12 hours, the solid product was collected and dissolved in hot aqueous ammonia. On filtering and cooling, the ammonium salt of *2-phenyliminomethyl*cyclo*pentanone-4′-sulphonic acid* separated in colourless, transparent prisms. The free acid, isolated by dissolving the salt in a little hot water, acidifying the solution, and allowing it to cool, separated in pale yellow needles (Found : S, 11·7. $C_{12}H_{13}O_4NS$ requires S, 12·0%).

Ethyl 1-Anilino-$\Delta^{1:2}$-cyclo*hexene-2-carboxylate.*—When a mixture of ethyl *cyclo*hexanone-2-carboxylate (4·2 g., prepared by the method of Kötz and Michels, *Annalen*, 1906, **350**, 210; 1908, **358**, 198) and aniline (2·3 g.) was kept over calcium chloride in an evacuated desiccator for a fortnight, the mixture solidified, and, after being pressed on porous porcelain and subsequently crystallised from methyl alcohol, *ethyl 1-anilino-*$\Delta^{1:2}$-cyclo*hexene-2-carboxylate* was obtained in good yield as colourless prisms, m. p. 58·5° (Found : N, 5·7. $C_{15}H_{19}O_2N$ requires N, 5·7%).

When the crude ester was rapidly heated to 265° and maintained at that temperature for a minute, the product solidified, and, after treatment with boiling benzene, tetrahydroacridone, identical in every way with a specimen prepared by the method of Tiedtke (*loc. cit.*), remained.

*9-Keto-*5 : 6 : 7 : 8 : 9 : *10-hexahydrophenanthridine.*—When a mixture of ethyl *cyclo*hexanone-2-carboxylate (4·2 g.) and aniline (2·3 g.) was boiled under reflux for 2 minutes, cooled, and kept for 6 hours, it partly solidified. The solid was washed with petroleum, and, after crystallising first from aqueous alcohol and then from benzene–petroleum, cyclo*hexanone-2-carboxyanilide* was isolated in short, colourless prisms, m. p. 105—105·5° (Found : N, 6·3. $C_{13}H_{15}O_2N$ requires N, 6·4%). When the crude product obtained by boiling the mixture of ethyl *cyclo*hexanone-2-carboxylate and aniline for 2 minutes was poured slowly into concentrated sulphuric acid (7 c.c.), the whole heated for 15 minutes on the steam-bath, and then poured into water, *9-keto-*5 : 6 : 7 : 8 : 9 : *10-hexahydrophenanthridine* separated. After crystallisation from 70% acetic acid, it was obtained in colourless plates, m. p. 267—268° (Found : N, 7·0. $C_{13}H_{13}ON$ requires N, 7·0%).

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