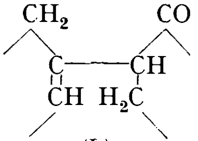
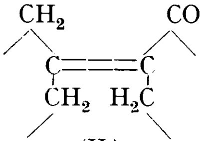
350. *Condensation Products of Dicyclic Ketones.*

By R. S. THAKUR.

MONOCYCLIC ketones give each a self-condensation product of only one type; *e.g.*, *cyclo*hexanone yields only the Δ^{β}-ketone, 2-*cyclo*hexenyl*cyclo*hexanone (I), and *cyclo*pentanone yields only the Δ^{α}-ketone, 2-*cyclo*pentylidene*cyclo*pentanone (II) (Wallach, *Ber.*, 1896,

29, 2963; *Annalen*, 1911, **381**, 95; Kon and Nutland, J., 1926, 3101). It is now shown that dicyclic ketones also behave in the same way on self-condensation; *e.g.*, *trans*-β-decalone gives only a Δ^{β}-ketone (as I), and *trans*-hexahydro-2-hydrindone yields only the Δ^{α}-ketone (III).


(I.)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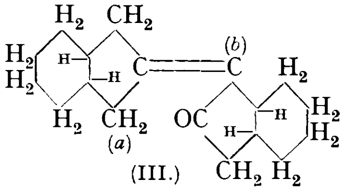
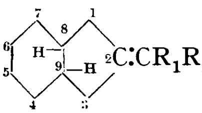

(III.)

The possibility of stereoisomerism in the compound (III) is not clear at first. Compounds of the type (IV) should exist in one form only (racemic), like the *trans*-hexahydro-2-hydrindol of Hückel and Friedrich (*Annalen*, 1926, **451**, 132), since no new centre of asymmetry is created at C_2 by the attachment of $:CR_1R_2$. This is the case, no geometrical isomerism having been observed in the α-methyl-*trans*-hexahydrohydrindylidene- and *trans*-hexahydrohydrindylidene-2-acetic acids (Kandiah, J., 1931, 933; Thakur, J., 1932, 2153, 2162). Hence, although the ring (*b*) in (III) is unsymmetrical about C_1 (thus corresponding to R_1R_2), the compound (III) should exist in one form only. Again, in compounds of the type (V), two forms are possible only if R_1 and R_2 are different or form an unsymmetrical ring. If they are similar or are replaced by a symmetrical ring [as by (*a*) in III], only one form should exist.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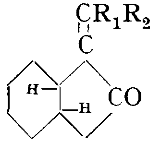
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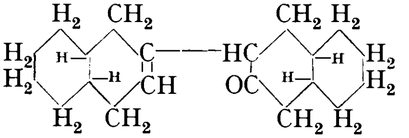
(VI.)

On the other hand, since *trans*-hexahydro-2-hydrindone is a racemic compound, the following combinations are possible on condensation: l_al_b, d_ad_b; l_ad_b, d_al_b. These two pairs will give two racemic compounds (compare Hückel, Danneel, Gross, and Naab, *Annalen*, 1933, **502**, 107). The only evidence for the existence of these two isomerides is the indefinite melting point of the condensation product ($C_{18}H_{26}O$). With the possible exception of the semicarbazone, all the other derivatives of (III) are more or less homogeneous. It is highly probable, too, that the isomerism of the semicarbazone is geometrical and not structural (compare Forster and Zimmerli, J., 1910, **97**, 2156; Wilson and Heilbron, J., 1912, **101**, 1482; Wilson and Macaulay, J., 1924, **125**, 841).

In the presence of sodium ethoxide, the rate of self-condensation of *trans*-hexahydro-2-hydrindone seems to be much greater than that of *cyclo*pentanone. No higher condensation products, such as $C_{15}H_{20}O$, are formed from three or more molecules of *cyclo*pentanone. The condensation of *trans*-hexahydro-2-hydrindone in the presence of dry hydrogen chloride gives a very small quantity of (III) and a *hydrocarbon* $(C_9H_{12})_n$ (probably $n = 3$).

In an attempt to convert *cis*-α-decalone into the *trans*-form, or vice versa, by heating with methyl-alcoholic sodium methoxide, Hückel and Brinkmann obtained a product which they named " bisdecalon " (*Annalen*, 1925, **441**, 34) and regarded as the primary addition product of two decalone molecules. In the present investigation, in which dry sodium ethoxide was used, no unchanged *trans*-β-decalone was left after one day (compare *cyclo*hexanone, of which the condensation is incomplete even after a long time; Wallach, *loc. cit.*), *trans*-β-decalol was obtained in 25—28% yield, and no identifiable condensation product was isolated. Analysis showed that the rosin-like mass obtained was not the condensation product formed from three molecules of the ketone, like the one formed from three molecules of *cyclo*hexanone (Wallach, *loc. cit.*). The fact that alcoholic sodium ethoxide converts $\Delta^{2\,(\text{or}\,1)}$-*trans*-octahydronaphthyl-*trans*-β-decalone into a viscous mass may account for the failure to obtain this compound in the above condensation.

The condensation of *trans*-β-decalone in the presence of dry hydrogen chloride proceeded rapidly and completely and two *chloro*-compounds, $C_{20}H_{31}OCl$, were isolated. From these, by the elimination of hydrogen chloride, a ketone, $C_{20}H_{30}O$, was obtained.

The ketone $C_{20}H_{30}O$ (J., 1932, 2128), m. p. 125—126°, gave only *trans-cyclo*hexane-1 : 2-diacetic acid as the final product of oxidation and therefore is probably the Δ^2-compound (VI).

EXPERIMENTAL.

Condensation of trans-*Hexahydro-2-hydrindone.*—(i) *In presence of dry hydrogen chloride.* The ketone (46 g.), cooled in ice, was saturated with the dry gas. After remaining at room temperature for 8 weeks, the product was poured into water, neutralised with sodium carbonate, and extracted with ether, and the residue steam-distilled to remove *trans*-hexahydro-2-hydrindone. The final reddish-brown viscous mass (1·6 g.) gave the oxime of *trans*-hexahydrohydrindylidene-2-*trans*-hexahydrohydrindone (III), m. p. 206—208° (J., 1932, 2152; m. p. 211—212°). From the unchanged substance, light petroleum (b. p. 40—60°) extracted a *hydrocarbon*, which crystallised from methyl alcohol in long thin needles, m. p. 116—118° [Found : C, 90·3; H, 9·8. $(C_9H_{12})_n$ requires C, 90·0; H, 10·0%].

(ii) *In presence of sodium ethoxide.* From a mixture of the ketone (14 g.) and dry sodium ethoxide (from 2·3 g. of sodium), after a few hours, no unchanged ketone was recovered on steam-distillation. The residue (13·5 g.) gave a crystalline oxime, m. p. 206—208°.

In another experiment, the residue, crystallised from methyl alcohol, gave a first crop, m. p. 100—105°, and 109—110° after recrystallisation.

Derivatives of trans-*Hexahydrohydrindylidene*-2-trans-*hexahydrohydrindone* (III).—The ketone (m. p. 100—105°) was converted by Allen's method (*J. Amer. Chem. Soc.*, 1930, **52**, 2955) into the 2 : 4-*dinitrophenylhydrazone*, a deep orange solid, m. p. 248° (decomp.) after crystallisation from chloroform–ethyl acetate (Found: C, 65·4; H, 6·9. $C_{24}H_{30}O_4N_4$ requires C, 65·7; H, 6·9%).

The *phenylhydrazone* was a colourless crystalline solid, m. p. 193—194° (decomp.) in the crude state and after crystallisation from ethyl acetate–alcohol (Found : C, 82·3; H, 9·0. $C_{24}H_{32}N_2$ requires C, 82·7; H, 9·3%).

The p-*nitrophenylhydrazone* was obtained as brick-red needles, m. p. 267° (decomp.) after darkening (Found : C, 73·2; H, 7·75. $C_{24}H_{31}O_2N_3$ requires C, 73·2; H, 8·0%).

The *semicarbazone*, formed by refluxing the ketone (m. p. 100—105°) and semicarbazide acetate in alcohol for 1 hour, separated at room temperature in colourless crystals. The m. p. varied in different preparations, 180°, 185—187°, 200—210° after sintering from 180°. The semicarbazone of m. p. 180° remained unchanged for several months, but after it had been kept in the steam-oven for a short time or boiled with light petroleum, the m. p. rose to 225—226° (decomp.). The crude semicarbazone crystallised from alcohol in needles, m. p. 234—235° (decomp.); crystals melting between 225° and 235° were often obtained (Found : C, 72·1; H, 9·25. $C_{19}H_{29}ON_3$ requires C, 72·3; H, 9·3%). Kandiah (J., 1931, 945) gives m. p. 140° (his analytical figures are calculated from a wrong formula $C_{18}H_{29}ON_3$).

The semicarbazone (m. p. 180°) was crystallised from benzene–petroleum. A few of the crystals were removed and found to have m. p. 182—183° (this observation could not be repeated in subsequent crystallisations, the semicarbazone, m. p. 225—235°, being always obtained); after 2 days, the whole mass was filtered off—it melted at 225—226°. The crude semicarbazone, therefore, consists mainly of the lower-melting form, which is converted into the higher-melting form on crystallisation or on warming.

Oxidation. The ketone (III) (m. p. 110—112°) in chloroform was treated with ozonised oxygen at 0°, the ozonide freed from the solvent and decomposed, and the product steam-distilled. The earlier portion of the distillate contained *trans*-hexahydro-2-hydrindone (semicarbazone, m. p. and mixed m. p. 245°); a colourless crystalline solid, filtered off from the later portion and washed with cold methyl alcohol, had m. p. 190° (decomp.), and mixed m. p. with authentic *trans*-hexahydro-2-hydrindone peroxide (J., 1932, 2166) 191—192°. From the residue in the distillation flask, hot water extracted *trans*-hexahydrohomophthalic acid, m. p. 160—161°.

Condensation of trans-β-*Decalone.*—(i) *In presence of dry hydrogen chloride.* The dry gas was passed through the ketone, cooled in ice, for an hour. The viscous product solidified on long standing or when seeded with the chloro-compound (below). Fractional crystallisation from petroleum (b. p. 60—80°) separated a less soluble *chloro*-compound, short prisms, m. p.

130—131° (Found: C, 74·7; H, 9·6. $C_{20}H_{31}OCl$ requires C, 74·4; H, 9·7%), from a more soluble *isomeride*, radiating spear-like needles, m. p. 118—119° (Found: C, 74·1; H, 9·65%). A mixture of the two melted at 109—112° (decomp.) after sintering.

Elimination of hydrogen chloride from the chloro-compounds. (*a*) The crude condensation product (5 g.) obtained above was refluxed with pyridine for 1½ hours. The product (b. p. 230°/9 mm.) gave a *semicarbazone* which separated from benzene in rhombic crystals, m. p. 207° (Found: C, 73·7; H, 9·7; N, 12·1. $C_{21}H_{33}ON_3$ requires C, 73·4; H, 9·7; N, 12·25%).

(*b*) The less soluble chloro-compound on distillation gave a colourless viscous solid, b. p. 228—230°/7 mm., which crystallised from petroleum in radiating needles and aggregates of prisms (Found: C, 83·7; H, 10·5. $C_{20}H_{30}O$ requires C, 83·8; H, 10·6%).

(ii) *In presence of sodium ethoxide.* (*a*) *trans*-β-Decalone (38 g.) was treated with dry sodium ethoxide (from 5·8 g. of sodium) at room temperature. From the product, after 8 days, *trans*-β-decalol (b. p. 110—112°/2 mm., m. p. 75°; 10·2 g.) was isolated. The residue, when kept under diminished pressure, frothed considerably and finally solidified (Found: C, 80·3; H, 10·3. "Bisdecalone," $C_{20}H_{32}O_2$, requires C, 79·0; H, 10·6%. $C_{20}H_{30}O$ requires C, 83·8; H, 10·6%. $C_{30}H_{44}O$ requires C, 85·7; H, 10·5%).

(*b*) In a similar experiment, after removal of *trans*-β-decalol (10 g. from 38 g. of the ketone), the residue was distilled up to 210°/1 mm. The distillate was a viscous oil (Found: C, 80·7; H, 10·25%). The undistilled residue solidified.

(*c*) An insufficiency of sodium ethoxide was used (from 0·5 g. instead of 3 g. of sodium, the theoretical amount for 19 g. of the ketone). After 8 days, unchanged *trans*-β-decalone (10 g.) and the condensation product (?) (8 g.) were obtained.

The rosin-like solid obtained in the above condensations could not be crystallised and gave no semicarbazone. With hydroxylamine hydrochloride and alcoholic sodium acetate solution, a compound, m. p. 255—256° (decomp.), insoluble in almost all solvents, was obtained in very poor yield (Found: C, 73·4; H, 10·1; N, 7·6%).

$\Delta^{2\,(\text{or}\,1)}$-trans-*Octahydronaphthyl*-2-trans-β-*decalone*.—The unhydrolysed residue obtained in the condensation of *trans*-β-decalone with ethyl bromoacetate or ethyl α-bromopropionate and zinc (J., 1932, 2128, 2142) has been again examined. By crystallisation from petroleum or methyl alcohol, in addition to the ketone of m. p. 125—126°, fractions melting over a wide range, 85—120°, were obtained, and ultimately a product, m. p. 75—80° (mixed m. p. with *trans*-β-decalol, 60°).

The semicarbazone of the higher-melting ketone had m. p. 212° (decomp.) after crystallisation from benzene; that of the lower-melting ketone (m. p. 75—85°) melted at 224—225° (decomp.).

The same *phenylhydrazone*, m. p. 153—154°, was obtained from both ketones (Found: C, 83·0; H, 9·6. $C_{26}H_{36}N_2$ requires C, 82·9; H, 9·65%).

The 2 : 4-*dinitrophenylhydrazone* of the ketone of m. p. 125—126° was an orange solid, m. p. 173—174°, and 175—176° after crystallisation from ethyl acetate (orange-yellow micro-crystals) (Found: C, 66·9; H, 7·3. $C_{26}H_{34}O_4N_4$ requires C, 66·9; H, 7·35%).

From a ketonic fraction of m. p. 83—120°, a crude 2 : 4-dinitrophenylhydrazone was obtained, m. p. 146—147°. Crystallised from ethyl acetate–alcohol, this gave lemon-yellow crystals, m. p. 194—195° (decomp.) (Found: C, 66·9; H, 7·3%), which, however, did not depress the m. p. (175—176°) of the compound mentioned above.

The p-*nitrophenylhydrazone* of the ketone of m. p. 125—126° formed yellow needles, m. p. 208° (decomp.) (Found: C, 73·8; H, 8·2. $C_{26}H_{35}O_2N_3$ requires C, 74·1; H, 8·4%). That of the ketone of m. p. 80—90° gave a first crop, m. p. 205° (decomp.) after sintering, which did not depress the m. p. of the preceding compound. A second crop had m. p. 191—193° after sintering.

Oxidation of $\Delta^{2\,(\text{or}\,1)}$-trans-*Octahydronaphthyl*-2-trans-β-*decalone*.—The ozonisation was carried out and the product worked up as described on p. 1479. The aqueous distillate gave no *trans*-β-decalone. The residue in the steam distillation flask was extracted with hot water. The filtered extract on concentration gave three crops, m. p. 156—160°, 146—153°, and 146—153°. On recrystallisation, *trans-cyclo*hexane-1 : 2-diacetic acid (m. p. and mixed m. p. 164—166°) was obtained from the first crop. Dianilide, m. p. 285° (Hückel and Friederich, *loc. cit.*, give m. p. 283°). The lower-melting acid, on conversion into the dianilide, gave that of *trans-cyclo*hexane-1 : 2-diacetic acid only (m. p. 280°); no indication of the presence of the dianilide of 1-carboxy-*trans-cyclo*hexane-2-propionic acid was obtained.

The oxidation product which did not dissolve in hot water yielded more *trans-cyclo*hexane-1 : 2-diacetic acid after further ozonisation. The still unchanged viscous residue was oxidised with hot nitric acid, giving more of the above acid (dianilide, m. p. 285°).

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IMPERIAL COLLEGE, LONDON, S.W. 7.

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