392. *The Synthesis of Polyterpenoid Compounds. Part II.*

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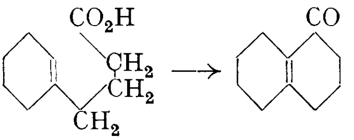
The type of method outlined in Part I (Cook and Dansi, this vol., p. 500) for the synthesis of completely hydrogenated polycyclic systems has been supplemented by an alternative method, illustrated by the example now described, which should prove extremely useful as a basis for the synthesis of substances closely related to the dicyclic sesquiterpenes, of perhydrophenanthrene derivatives, and ultimately, of sterol-like compounds. We are investigating the extent to which the new method is of general application, and we propose to develop it in the manner indicated.



(I.) (II.)

The chloride of γ-Δ^1-cyclo*hexenylbutyric acid* (I), obtained by condensation of β-Δ^1-*cyclo*hexenylethyl bromide with ethyl potassiomalonate, with subsequent hydrolysis and decarboxylation, was cyclised by stannic chloride to $\Delta^{9:10}$-α-octalone (II), the properties of which were in good agreement with those cited by Hückel and Naab (*Annalen*, 1933, **502**, 153) for this ketone, which these authors isolated from the products of chromic acid oxidation of $\Delta^{9:10}$-octalin.

Many examples of condensations between acid chlorides and *cyclo*olefins have been recorded since the reaction was introduced by Darzens (*Compt. rend.*, 1910, **150**, 707), but we believe that the reaction has not hitherto been used for ring formation. The recent failures of Bradfield, Jones, and Simonsen (J., 1934, 1810) and Barrett, Cook, and Linstead (this vol., p. 1067) to obtain dicyclic ketones by cyclisation of a carboxylated side chain on to a *saturated* ring are not surprising.

Experimental.

β-(Δ^1-cyclo*Hexenyl)ethylmalonic Acid.*—In the preparation of β-Δ^1-*cyclo*hexenylethyl bromide (Cook and Dansi, *loc. cit.*) better results were obtained by dehydrating the intermediate ethyl *cyclo*hexanol-1-acetate with thionyl chloride in pyridine (compare Linstead and Meade, J., 1934, 942) : Thionyl chloride (60 c.c.) was added during 2 hours, with mechanical stirring, to an ice-cold mixture of ethyl *cyclo*hexanol-1-acetate (150 g.), pure pyridine (165 g.), and anhydrous ether (340 c.c.). Stirring and cooling were continued for another 2 hours, and the ethyl Δ^1-*cyclo*hexenylacetate (122 g.; 90% yield) was isolated in the usual way.

β-Δ^1-*cyclo*Hexenylethyl bromide (30 g.), diluted with benzene (60 c.c.), was added to ethyl potassiomalonate prepared from ethyl malonate (48 g.), powdered potassium (7 g.), and benzene (160 c.c.). The whole was heated on the water-bath for 120 hours, and the substituted malonic ester (b. p. 148°/1—1·5 mm.; 24·9 g.; 58% yield) isolated in the normal manner. The yield was only 31% when heating was restricted to 20 hours. This ester was hydrolysed by boiling alcoholic potash in 2 hours; the crude malonic acid was then obtained as a brown oil which partly solidified when kept in the ice-chest. After being drained on a tile, and recrystallised from *cyclo*hexane, β-(Δ^1-cyclo*hexenylethyl)malonic acid* formed a colourless crystalline powder, m. p. 123—124° (Found : C, 62·4; H, 7·8. $C_{11}H_{16}O_4$ requires C, 62·3; H, 7·6%).

γ-Δ^1-cyclo*Hexenylbutyric Acid* (I).—This was obtained in 65% yield when the crude malonic acid was heated at 180° for ½ hour, and distilled in a vacuum. γ-Δ^1-cyclo*Hexenylbutyric acid* formed a colourless liquid, b. p. 122—125°/0·8 mm., which became yellow on standing (Found : C, 70·7; H, 10·1. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%). Its p-*phenylphenacyl* ester formed small colourless needles, m. p. 79·5—81° (Found : C, 78·8; H, 7·9. $C_{24}H_{26}O_3$ requires C, 79·5; H, 7·25%).

$\Delta^{9:10}$-α-*Octalone* (II).—Thionyl chloride (4 g.) was slowly added to an ice-cold mixture of the butyric acid (I) (5·6 g.), pyridine (2·7 g.), and dry ether (30 c.c.) (compare Carré and Liebermann, *Compt. rend.*, 1934, **199**, 1423). A little ethereal hydrogen chloride was then added to complete the precipitation of the pyridine as hydrochloride, and the liquid was filtered. After removal of the solvent, the residual acid chloride was heated briefly at 100° under reduced pressure, and then mixed with carbon disulphide (10 c.c.) and added gradually to a mixture of anhydrous stannic chloride (8·5 g.) and carbon disulphide (20 c.c.), the temperature being maintained at — 7° to — 10°. The whole was kept in the freezing mixture for an hour, then at room temperature for 3 hours, and decomposed with ice. The carbon disulphide solution having been dried, dimethylaniline (4·2 g.) was added, the solvent removed, and the residue heated at 180—190° for 3 hours. The product was extracted with ether and dilute hydrochloric acid, and the ketone isolated by distillation (yield, 2·6 g.), b. p. about 140°/9 mm. That elimination of hydrogen chloride from the intermediate chloro-ketone had given the αβ-unsaturated ketone (II), and not one of the two alternative ketones, was shown by the optical exaltation of the compound, and also by the agreement between the m. p.'s of the derivatives and those of the corresponding derivatives of $\Delta^{9:10}$-α-octalone (Hückel and Blohm, *Annalen*, 1933, **502**, 135; Hückel and Naab, *loc. cit.*). Our ketone had $d_{4°}^{14°}$ 1·000, $n_D^{14°}$ 1·4996, whence $[R_L]_D = 44·12$ (calc., 43·52). The oxime had m. p. 144—145° (benzoyl derivative, m. p. 130·5—131·5°), and the semicarbazone had m. p. 242—243°.

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