243. *Experiments on the Synthesis of Substances related to the Sterols. Part XVII. 8-Methylhydrindan-1-one.*

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Owing to the anticipation of work already published in part, an account is submitted of the synthesis of 8-methylhydrindanone from ethyl 2-methyl*cyclo*hexanone-2-carboxylate. A side chain is introduced by means of the Grignard reaction and the product is suitably modified so as to obtain a dicarboxylic acid, from which the ketone is readily obtained by the known method.

IN a paper submitted on December 14th, 1936, and published in the January number of the *Journal* (this vol., p. 60), we described the first stages of a new method for the construction of ketones containing angular methyl groups and stated that further investigation of the subject was in progress. The remaining processes of a more routine character were studied without undue loss of time and are described below.

In the meantime, Kon, Linstead, and Simons, in a paper (this vol., p. 814) submitted six weeks after the publication of ours, have described the same method (ethoxyl instead of methoxyl) and an acknowledgment is contained in a footnote. We fully recognise the independent nature of the work of these authors and at the same time claim as much for our own. A statement that the ketone had been made was included in a contribution to a discussion at the Chemical Society on May 20th. Consequently we are compelled to submit an account of the completion of this part of our researches leading to the preparation of a ketone first described by Chuang, Tien, and Ma (*Ber.*, 1936, **69**, 1494). In view of the recent publication of Kon, Linstead, and Simons (*loc. cit.*) a further theoretical description is unnecessary. It only remains to add that the process of these authors for the dehydration of the carbinol is superior to ours and on the other hand our overall yield in the three last stages is about twice as great as theirs.

EXPERIMENTAL.

*Ethyl 2-Methyl-1-γ-methoxypropyl*cyclo*hexane-2-carboxylate.*—The divergence in the analytical figures from the anticipated values as previously recorded (this vol., foot of p. 65) was actually due to contamination with a small amount of the carbinol. The hydrogenated material (*loc. cit.*) (4·9 g.) was heated with potassium hydrogen sulphate (10 g.) for 3 hours at 180—190°, and the recovered material distilled (4·5 g.) at 138—142°/12 mm.; $n_{\rm D}^{16^\circ}$ 1·4582. Hydrogenation was effected as before in methyl alcohol (70 c.c.) with palladised strontium carbonate (6 g.) under pressure for 16 hours. The saturated material (4·2 g.) was a colourless mobile oil, b. p. 138—140°/12 mm., $n_{\rm D}^{14^\circ}$ 1·4588 (Found: C, 69·1; H, 10·7. $C_{14}H_{26}O_3$ requires C, 69·4; H, 10·7%).

Ethyl 2-*Methyl*-1-γ-*hydroxypropyl*cyclo*hexane*-2-*carboxylate*.—The foregoing compound (4·0 g.) was dissolved in acetic anhydride (25 c.c.) saturated below 0° with hydrogen bromide and the solution was left for 5 days in the ice-chest. The resulting clear, almost colourless solution was mixed with ice-water and extracted with ether. The extract was well washed with sodium carbonate solution, dried, and evaporated. The crude neutral material (4·2 g.) contained bromine and was heated with anhydrous potassium acetate (7 g.) in glacial acetic acid (10 c.c.) on the steam-bath for 5 hours. The recovered material still contained bromine and the treatment with potassium acetate was repeated under reflux. The halogen-free product (4·07 g.) was refluxed for 6 hours with 2·5% methyl-alcoholic potassium hydroxide (50 c.c.); the neutral material (3·3 g.), isolated in the usual way, distilled (2·72 g.) as a colourless limpid oil at 160—165°/13 mm.; $n_{\rm D}^{16^\circ}$ 1·4725 (Found: C, 68·5; H, 10·5. $C_{13}H_{24}O_3$ requires C, 68·4; H, 10·5%).

2-*Methyl*cyclo*hexane*-2-*carboxylic*-1-β-*propionic Acid*.—The above ester was not readily hydrolysed. The ester (2·6 g.) was refluxed for 30 hours with baryta (3·7 g.; large excess) in 50% methyl alcohol (30 c.c.), and the product separated into acidic (1·3 g.) and neutral (1·1 g.) portions. The latter was refluxed for 30 hours with alcoholic potassium hydroxide (2 g. of potassium hydroxide in 10 c.c.), and the acidic material recovered added to that previously obtained (total, 2·18 g.); it was a colourless syrup which did not crystallise. Oxidation was effected with the theoretical amount of potassium permanganate (2·28 g.) in water, added to a solution of the hydroxy-acid (2·18 g.) in aqueous sodium carbonate (1·3 g. in 4 c.c.). The mixture was left at room temperature until the colour of the permanganate disappeared (2 days), filtered, and the hot water washings of the residue added to the filtrate. After acidification the dibasic acid was extracted with ether and recovered (1·88 g.) as an exceedingly viscous, colourless syrup. It showed no signs of crystallisation after 2 days in the ice-chest and was characterised by the following experiment.

8-*Methylhydrindan*-1-*one*.—The above dibasic acid (1·88 g.) was distilled with baryta (120 mg.) at 300—320° until reaction appeared to be complete (*ca.* 1 hour) and distillate and residue were worked up for neutral product in the normal way by extraction with ether. The crude product (1·14 g.) was distilled in a vacuum; the ketone (0·67 g.; 50%), collected at 93—95°/18 mm., solidified to a colourless waxy solid; it had a pronounced odour of camphor and could just be melted by the warmth of the hand (Found: C, 78·8; H, 10·6. $C_{10}H_{16}O$ requires C, 78·9; H, 10·5%). The *semicarbazone* had m. p. 221—222° after one recrystallisation from aqueous alcohol (Found: C, 63·5; H, 9·1. $C_{11}H_{19}ON_3$ requires C, 63·2; H, 9·1%).

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