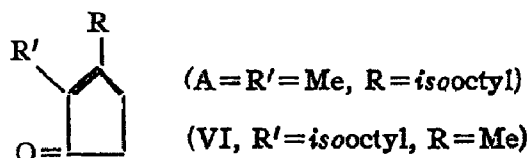


SYNTHESIS OF ISOOCTYLMETHYLCYCLOPENTADIENE

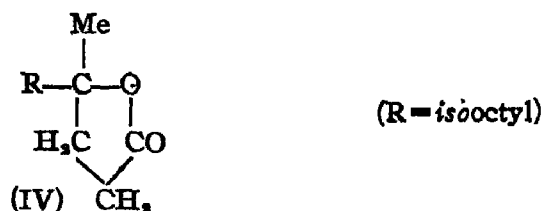
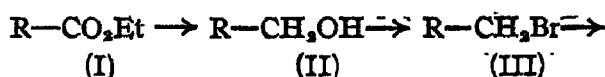
BY PROVAS KUMAR DUTTA

A synthesis of 2-(methylheptyl)-3-methyl- Δ^2 : δ -cyclopentadiene has been described.

Attention was directed to the synthesis of certain methylcyclopentenones with the isooctyl side-chain attached to the carbon atom adjacent to that carrying the methyl group, of which the two following were the two (VI, A) immediate objectives.



Earlier attempts to synthesise this ketone (A) through the oxidation of the corresponding cyclopentene with selenium dioxide failed (Rydon, *J. Chem. Soc.*, 1940, 1546) and preliminary studies to build up similar cyclopentenone derivatives from 1:4-diketones have proved futile (Mitter and Dutta, this *Journal*, 1948, 26, 306). Experiments were next undertaken to synthesise (VI) according to the interesting method which has been recently developed for the preparation of substituted cyclopentenones through distillation of γ -lactones with phosphorus pentoxide (Frank *et al.*, *J. Amer. Chem. Soc.*, 1944, 66, 4).

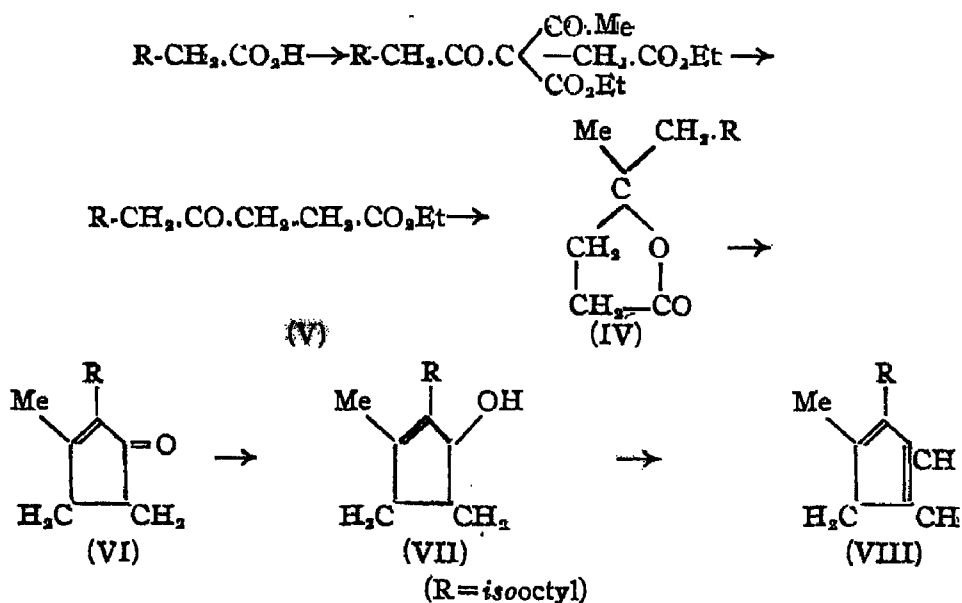


sec-isooctyl iodide is converted into cyanide which passes into the ester (I) directly on treatment with alcohol and sulphuric acid. Reduction of this ester with alcohol and sodium gives (II) which passes into the bromide (III) on refluxing with sulphuric and hydrobromic acids. The Grignard's complex, prepared from this bromide in presence of equivalent amount of methyl iodide, reacts smoothly with ethyl laevulinate in dilute ethereal solution in the cold. From the reaction mixture the lactone (IV) is obtained in rather a poor yield. The synthesis of the lactone has been carried out more successfully by employing the well known method developed by G. M. Robinson for the synthesis of long-chain keto-acids. The starting material in this case is *sec*-isooctyl-acetic acid (Dutta, this *Journal*, 1942, 19, 78). The acid chloride condenses smoothly with the sodio-salt of ethyl acetosuccinate. The crude condensation product is hydrolysed through prolonged shaking at the ordinary temperature (Chuang *et al.*, *Ber.*, 1936, 69, 1492). The keto-acid is isolated as its ethyl ester (V) which reacts smoothly with methylmagnesium iodide. The desired lactone (IV) is obtained in a good yield on hydrolysis with alkali and subsequent lactonisation on warming with dilute sulphuric acid. On distillation of the lactone over phosphorus pentoxide, the cyclopentenone

derivative (VI) is obtained in a moderate yield. The structure of the unsaturated *cyclopentenone* (VI) has been assigned on the basis of similar observations on the synthesis of dihydrojasnone from the lactone prepared from *isohexyl iodide* and ethyl laevulinate (Frank *et al.*, *loc. cit.* Dutta and Sen Gupta, this *Journal*, 1948, 25, 213), and also from the later observations of Frank *et al.* (*J. Amer. Chem. Soc.*, 1948, 60, 1379) where it has been definitely established that in the case of γ -lactones having a methylene group and a methyl group available for the formation of the *cyclopentenone* ring, the reaction always proceeds in the direction where only the methylene group is involved.

Reduction of the ketone with aluminium isopropoxide affords the unsaturated alcohol (VII). This is converted into the chloride with thionyl chloride in presence of pyridine and the chloro compound is heated with excess of dimethylaniline to give the doubly unsaturated compound (VIII). Attempts to introduce different groups at the methylene group through the potassium salt of the *cyclopentadiene* (VIII) have met with failure so far.

The whole scheme of work can be drawn up as follows:—



EXPERIMENTAL

Ethyl 2:6-Dimethylheptate (I).—A mixture consisting of methylheptyl cyanide (34 g.), rectified spirit (47 c.c.), alcohol (47 c.c.) and concentrated sulphuric acid (39 c.c.) was heated under reflux for 12 hours in an oil-bath. The resulting ester was cooled, diluted with water and extracted with ether. A mobile liquid passed over at 80°-85°/12 mm. having a sweet smell, yield 25 g. (Found: C, 71.6; H, 11.4. $\text{C}_{12}\text{H}_{24}\text{O}_2$ requires C, 72.0; H, 12.0 per cent).

2:6-Dimethylheptyl Alcohol (II).—Sodium (21 g.) was placed in a three-necked flask and the above ester (25 g.) and alcohol, dried over magnesium methoxide, were next introduced. After the vigorous reaction had subsided, it was refluxed in an oil-bath until the whole of sodium had reacted. It was cooled, diluted considerably with

water and extracted with ether. On working up in the usual way the desired alcohol (13 g.) passed over at 90° - $95^{\circ}/18$ mm.

2:6-Dimethylheptyl Bromide (III).—A mixture of 2:6-dimethylheptyl alcohol (13 g.), hydrobromic acid (48%, 45 g.) and concentrated sulphuric acid (11.5 g., d 1.84) was boiled under reflux for 2 hours. It was diluted with water and the bromide layer separated, and washed with a little cold concentrated sulphuric acid to remove the unchanged alcohol. The bromide (12 g.) was collected at $85^{\circ}/18$ mm. as a heavy liquid.

Lactone of δ -(2:6-Dimethylhexyl)- γ -methyl- γ -hydroxyvaleric Acid (IV).—Magnesium (4 g.) was covered with ether (20 c.c.) and methyl iodide (2 c.c.) was added to start the reaction. Next it was warmed and to the hot solution the above bromide (6 g.) in ether (25 c.c.) was slowly added. The mixture was refluxed gently for some time more until there was no perceptible reaction. Ethyl laevulinate (8 g.), dissolved in ether (50 c.c.), was cooled in an ice-bath and to this the above Grignard's complex was added gradually with shaking. It was allowed to stand for further one hour in the ice-bath and at ordinary temperature for another half-an-hour. The product was then decomposed with ice and hydrochloric acid and isolated by means of ether; it was dried (Na_2SO_4), ether removed and the residual liquid distilled in *vacuo*. The unchanged bromide and the ethyl laevulinate were collected as a forerun and the desired lactone in a poor yield at 135° - $140^{\circ}/6$ mm., yield 1.5 g. (Found: C, 73.8; H, 11.02. $\text{C}_{14}\text{H}_{26}\text{O}_2$ requires C, 74.4; H, 11.5 per cent).

Methylheptylacetic Acid.—Methylheptyl iodide (45 g.) was condensed with ethyl malonate (45 g.) in presence of sodium (4.5 g.) in alcohol (80 c.c.) in the usual way. It was worked up and the desired ester was obtained (b.p. $128^{\circ}/4$ mm.), yield 39 g. It was hydrolysed by refluxing the ester (25 g.) with caustic potash (15 g.) in water (15 c.c.) and rectified spirit (60 c.c.) for 6 hours. Alcohol was removed (water-bath) and the dibasic acid was obtained on acidification and subsequent extraction with ether. The residue left after the removal of the solvent was heated (oil-bath, 180° - 190°) for half-an-hour when decarboxylation was complete. The acid was isolated by vacuum distillation, b.p. $136^{\circ}/13$ mm., yield 15 g.

Methylheptylacetyl Chloride.—Methylheptylacetic acid (46 g.) was mixed with phosphorus trichloride (12 c.c.) and the resulting mixture was left overnight. Next it was heated on the water-bath for 2 hours. The clear upper layer was decanted off and distilled, when the acid chloride passed over at 90° - $100^{\circ}/14$ mm., yield 46 g.

Condensation of Ethyl Acetosuccinate and Methylheptylacetyl Chloride: Ethyl δ -Methylheptyl- γ -ketovalerate (V).—Sodium (6.2 g.) was molecularised and was taken under ether. This was cooled in ice and ethyl acetosuccinate (58 g.) was added dropwise. The mixture was kept overnight when a clear solution was obtained. Next day it was again cooled in ice and the acid chloride (46 g.) was added dropwise with occasional shaking. When the addition was complete, the mixture was refluxed (water-bath) for 2 hours. There was very little separation of sodium chloride. It was cooled and extracted with ether. The solvent was removed and it was directly employed for the next operation. The crude condensation product (100 g.), obtained from the previous reaction, was shaken with a mixture of distilled water (1800 c.c.), caustic potash (76 g.) and rectified spirit (900 c.c.) for 30 hours in a mechanical shaker. The turbid solution thus produced was neutralised with H_2SO_4 (75 g.) and then evaporated.

on the water-bath to remove alcohol. The residue was then strongly acidified and extracted with ether. After removal of ether, the remaining liquid was again hydrolysed by refluxing with caustic soda solution (660 c.c., 2*N*) on a water-bath for 3 hours. The solution was again acidified and extracted with ether. The residue after removal of ether was heated (water-bath) for half-an-hour. It was dried in *vacuo* and esterified with a cooled mixture of alcohol (150 c.c.) and concentrated sulphuric (9 c.c.) for 15 hours. The ester (25 g.) was isolated in the usual manner, b.p. 130°-132°/3 mm. (Found: C, 69.7; H, 10.84. $C_{15}H_{26}O_2$ requires C, 70.3; H, 10.94 per cent).

δ-Methylheptyl-γ-methyl-γ-valerolactone (IV).—Grignard's complex, prepared from magnesium (3.5 g.) and methyl iodide (15 c.c.), was added to the above keto-ester (25 g.) in dry ether (150 c.c.), cooled in a freezing mixture. The reaction mixture was allowed to stand for 2 hours and then decomposed with ice and ammonium chloride, acidified and extracted with ether. The residue after removal of the solvent was heated with alcoholic caustic potash solution (100 c.c., 10%) on the water-bath for 1 hour. The alcohol was removed and the ethereal extract of the alkaline solution containing the neutral fraction, if any, was rejected. The main alkaline layer was acidified and the mixture refluxed for 1 hour with dilute sulphuric acid (100 c.c., 10%). Finally it was extracted (ether), the ethereal extract washed with sodium bicarbonate solution and worked up as usual. A viscous liquid (18 g.) boiled at 125°-130°/3 mm. (Found: C, 74.4; H, 11.5. $C_{14}H_{26}O_2$ requires C, 74.3; H, 11.5 per cent).

2-Methylheptyl-3-methyl- Δ^2 -cyclopenten-1-one (VI).—The above lactone (8 g.) was mixed with P_2O_5 (4 g.) in a Claisen flask and heated in *vacuo* (oil-bath, 140°-150°) when a vigorous reaction took place and the whole mass turned dark brown. A mobile liquid (3 g.) passed over at 126°-134°/11 mm. On redistillation it came over at 126°-130°/11 mm. It has a characteristic smell. (Found: C, 79.9; H, 11.8. $C_{14}H_{24}O$ requires C, 80.5; H, 11.6 per cent).

2-Methylheptyl-3-methyl- Δ^2 -cyclopenten-1-ol (VII).—The above ketone (5 g.) was reduced with aluminium isopropylate, prepared from aluminium (3 g.) in isopropyl alcohol (60 c.c.) in the usual way. During distillation further isopropyl alcohol (40 c.c.) was added. The temperature of the oil-bath was kept at 90°-110°. On working up in the usual way the unsaturated alcohol was obtained boiling at 122°-124°/7 mm. having rather an unpleasant odour, yield 3.5 g. (Found: C, 79.8; H, 11.9. $C_{14}H_{26}O$ requires C, 80.0; H, 12.1 per cent). Attempts to prepare a phenylurethane derivative failed.

2-Methylheptyl-3-methyl- $\Delta^{2,5}$ -cyclopentadiene (VIII).—The above alcohol (3 g.) was dissolved in freshly distilled dimethylaniline (8 c.c.) and cooled. To this was added thionyl chloride (2 c.c.) when the mass turned deep brown. Next, excess thionyl chloride was removed in a high vacuum and the residue was heated in an oil-bath at 180°-190° for half-an-hour. On working up the diene was obtained as a clear, colorless oil boiling at 92°/2 mm., yield 1.2 g. (Found: C, 86.6; H, 12.1. $C_{14}H_{24}$ requires C, 87.5; H, 12.5 per cent).

The author's thanks are due to Dr. P. C. Dutta for his valuable help in this piece of investigation.