443. *Terpene Compounds. Part XII.* The Synthesis of (±)-Cryptone and Related Compounds.*

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(±)-Cryptone (V; R = Me) has been prepared by reduction of the enol isobutyl ether (IV; R = Me, R′ = OBu^i) with lithium aluminium hydride. In an analogous manner, its homologues (V; R = $CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe_2$ and $CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2$) have been synthesised, and a preliminary account of their reaction with methylmagnesion iodide is recorded.

(±)-Cryptone is formed by racemisation[1] of the corresponding optically active ketones which occur in a variety of essential oils.[2] Although several methods[3] are available for its synthesis, the product is often contaminated with isomers and its correspondence

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* Part XI, *J.*, 1963, 62.

[1] Cooke and Macbeth, *J.*, 1936, 1411; Gillespie and Macbeth, *J.*, 1939, 1531.

[2] Cahn, Penfold, and Simonsen, *J.*, 1931, 1366; Berry, Macbeth, and Swanson, *J.*, 1937, 1448; Wienhaus and Striegler, *Schimmel's Report*, 1937, p. 91.

[3] Wallach, *Annalen*, 1907, **356**, 235; 1908, **359**, 270; Birch, *J.*, 1946, 593; Frank and McPherson, *J. Amer. Chem. Soc.*, 1949, **71**, 1388; Lewis, *J.*, 1951, 2765; Rao and Dev, *J. Indian Chem. Soc.*, 1956, **33**, 539.

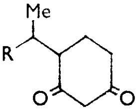
with that obtained from natural sources has not been fully established. We now report a synthesis of pure (±)-cryptone.

Cyanoethylation[4] of ethyl isopropylacetoacetate gave the ester (I), which on hydrolysis and elimination of carbon dioxide furnished the acid (II; R = H). The corresponding ethyl ester (II; R = Et), on cyclisation with sodium hydride,[5] afforded the known[6]

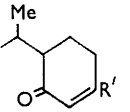
$$\underset{\text{(I)}}{\mathrm{Me{\cdot}CO{\cdot}CPr^i(CO_2Et){\cdot}CH_2{\cdot}CH_2{\cdot}CN}} \qquad \underset{\text{(II)}}{\mathrm{Me{\cdot}CO{\cdot}CHPr^i{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H}}$$

4-isopropylcyclohexane-1,3-dione (III; R = Me). This was converted in the usual way[7] into the enol isobutyl ether (IV; R = Me, R′ = OBu^i). Reduction with lithium aluminium hydride then gave the unsaturated ketone (V; R = Me) which was identical with (±)-cryptone in physical and chemical properties and in ultraviolet light absorption.

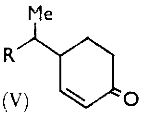
(III)



(IV)



(V)



We have extended our synthesis to the higher ketones (V where R = $[CH_2]_3{\cdot}Pr^i$ and $CH_2{\cdot}CH_2{\cdot}CH{:}CHMe_2$). In line with previous work,[6] diethyl 1,5-dimethylhexylmalonate was condensed with 4-diethylaminobutan-2-one methiodide,[8] giving the ester (VI; R = $[CH_2]_3{\cdot}Pr^i$) in good yield. This on hydrolysis in the usual way yielded the keto-acid (VII; R = $[CH_2]_3{\cdot}Pr^i$, R′ = H). The derived ethyl ester on treatment with sodium ethoxide[6] gave the diketone (III; R = $[CH_2]_3{\cdot}Pr^i$), which could not be distilled without decomposition. On treatment with phosphorus trichloride[9] the diketone gave the chloroketone (IV; R = $[CH_2]_3{\cdot}Pr^i$, R′ = Cl), which on catalytic reduction afforded a saturated ketone,. identical with 2-(1,5-dimethylhexyl)cyclohexanone prepared by an unequivocal method that will be described later. The corresponding enol isobutyl ether, obtained as usual,[7] was reduced by lithium aluminium hydride to the unsaturated ketone (V; R = $[CH_2]_3{\cdot}Pr^i$) (2,4-dinitrophenylhydrazone, m. p. 114°).

$$\underset{\text{(VI)}}{\mathrm{CHMeR{\cdot}C(CO_2Et)_2{\cdot}CH_2{\cdot}CH_2{\cdot}COMe}} \qquad \underset{\text{(VII)}}{\mathrm{CHMeR{\cdot}CH(CO_2R'){\cdot}CH_2{\cdot}CH_2{\cdot}COMe}}$$

In an analogous manner, ethyl 1,2-dimethylhex-4-enylmalonate was converted by a similar sequence into the unsaturated ketone (V; R = $CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2$) (2,4-dinitrophenylhydrazone, m. p. 118°). The same ketone had been prepared by another route, by Mukherji and Bhattacharyya[10] who were unable to obtain a crystalline derivative. The constitutions assigned to the ketones (V; R = $[CH_2]_3{\cdot}Pr^i$ and $CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2$) are based on analogy with the formation of cryptone outlined above. In support of this the ultraviolet absorption spectra of the ketones and their derivatives closely resemble those of cryptone and its derivative. Moreover, the two higher ketones (V) are reduced catalytically to the same saturated ketone, identical with a specimen obtained by rational synthesis that will be described later.

The ketone (V; R = $[CH_2]_3{\cdot}Pr^i$) reacted with methylmagnesium iodide under the conditions described for cryptone,[11] giving the alcohol (VIII; R = $[CH_2]_3{\cdot}Pr^i$), which

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[4] Cf. Bruson, " Organic Reactions," John Wiley, New York, 1949, Vol. V, p. 80.

[5] Cf. Conroy, *J. Amer. Chem. Soc.*, 1952, **74**, 3049.

[6] Bardhan, De, and Datta, *J.*, 1951, 3195.

[7] Frank and Hall, *J. Amer. Chem. Soc.*, 1950, **72**, 1648; Seifert and Schinz, *Helv. Chim. Acta*, 1951, **34**, 728.

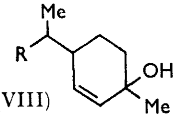
[8] du Feu, McQuillin, and Robinson, *J.*, 1937, 56; Wilds and Shunk, *J. Amer. Chem. Soc.*, 1943, **65**, 472.

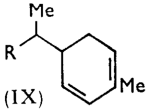
[9] Crossley and Le Sueur, *J.*, 1902, **81**, 675, 821; 1903, **83**, 117.

[10] Mukherji and Bhattacharyya, *J. Amer. Chem. Soc.*, 1953, **75**, 4700; cf. Birch and Mukherji, *J.*, 1949, 2531.

[11] Galloway, Dewar, and Read, *J.*, 1936, 1597.

was dehydrated by phosphorus oxychloride[12] to the cyclic diene (IX; $R = [CH_2]_3{\cdot}Pr^i$). Similarly the ketone (V; $R = CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2$) afforded the known[10] alcohol (VIII;


(VIII)


(IX)

$R = CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2$) and thence the unsaturated hydrocarbon (IX; $R = CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2$), having the ultraviolet absorption spectra of natural zingiberene[13] which it resembled in most other respects, although complete identity is not claimed.

EXPERIMENTAL

Cyanoethylation of Ethyl Isopropylacetoacetate.—Ethyl isopropylacetoacetate (25 g.), acrylonitrile (9 g.), and a 50% solution of potassium hydroxide in methanol (1 c.c.) were shaken at room temperature for 3 days. The product was diluted with an equal volume of chloroform, and the organic layer was separated, washed with water, dried and distilled. *Ethyl α-(2-cyanoethyl)-α-isopropylacetoacetate* (I) (9 g.) had b. p. 137—139°/5 mm. (Found: C, 63·8; H, 8·3. $C_{12}H_{19}NO_3$ requires C, 64·0; H, 8·4%). It gave no colour with alcoholic ferric chloride.

4-*Isopropyl*-5-*oxohexanoic Acid* (II; R = H).—The foregoing nitrile (7 g.), hydrochloric acid (40 c.c.), and acetic acid (10 c.c.) were refluxed for 10 hr. The excess of acetic acid was then removed, the residue extracted with ether, and the ethereal solution washed, dried, and distilled, giving 4-*isopropyl*-4-*oxohexanoic acid* (II; R = H) (3·7 g.), b. p. 147—149°/5 mm. (Found: C, 62·6; H, 9·2. $C_9H_{16}O_3$ requires C, 62·8; H, 9·3%). A semicarbazone could not be prepared under the usual conditions. The *ethyl ester* (prepared in ethanolic hydrogen chloride), b. p. 98—100°/5 mm. (Found: C, 65·8; H, 9·9. $C_{11}H_{20}O_3$ requires C, 66·0; H, 10·0%), did not form a semicarbazone.

4-*Isopropylcyclohexane*-1,3-*dione* (III; R = Me).—The preceding ethyl ester (25·6 g.), powdered sodium hydride[5] (6·8 g.), benzene (120 c.c.), and alcohol (0·5 c.c.) were refluxed in an atmosphere of nitrogen with stirring for 2 hr. The product was cooled in ice, then decomposed with ice-cold water, and the alkaline solution was separated, cooled, and acidified with dilute hydrochloric acid. The dione (22 g.), on purification from alcohol, had m. p. 106° (lit.,[6] m. p. 106—107°) (Found: C, 70·2; H, 9·3. Calc. for $C_9H_{14}O_2$: C, 70·1; H, 9·1%). Most of the dione required for this work was more conveniently prepared by Bardhan, De, and Datta's method.[6]

3-*Isobutoxy*-6-*isopropylcyclohex*-2-*enone* (IV; R = Me, R′ = OBu^i).—The diketone (III; R = Me) (13 g.), isobutyl alcohol (15 c.c.), benzene (60 c.c.), and toluene-*p*-sulphonic acid (0·5 g.) were refluxed for 14 hr. with removal of the water formed. The *ether*, isolated in the usual way (13·2 g.), had b. p. 139—141°/5 mm. (Found: C, 74·1; H, 10·4. $C_{13}H_{22}O_2$ requires C, 74·3; H, 10·5%). It gave no ferric chloride colour.

(±)-*Cryptone* (V; R = Me).—Lithium aluminium hydride (2 g.) was kept under dry ether (70 c.c.) and a solution of the ether (IV; R = Me, R′ = OBu^i) (13·2 g.) in ether (25 c.c.) was introduced at such a rate as to produce gentle refluxing; the whole was heated on the steam-bath for 1 hr. to complete the reaction, then cooled in a freezing mixture. Cold water (20 c.c.) was added, followed by an excess of cold dilute sulphuric acid. (±)Cryptone (7·8 g.) formed a colourless liquid having characteristic smell and b. p. 102—105°/17 mm. It readily furnished a semicarbazone, plates (from methyl alcohol), m. p. 196—196·5° (decomp.) (Found: C, 61·4; H, 8·7. Calc. for $C_{10}H_{17}N_3O$: C, 61·5; H, 8·7%). Gillespie and Macbeth[1] give m. p. 188°. The pure ketone regenerated from the semicarbazone had b. p. 103°/17 mm., d_4^{32} 0·9311, n_D^{32} 1·4790, $[R_L]_D$ 42·07 (Calc., 41·10), $\lambda_{max.}$ 227, 313 mμ (log ε 4·06, 1·67) (Found: C, 78·1; H, 9·9. Calc. for $C_9H_{14}O$: C, 78·2; H, 10·1%). Gillespie and Macbeth[1] give d_{30}^{30} 0·9393, n_D^{20} 1·4810. Cooke and Macbeth[1] give $\lambda_{max.}$ 226·3, 314 mμ (log ε 4·1, 1·56). It gave also a 2,4-dinitrophenylhydrazone, orange-red plates (from alcohol), m. p. 136—136·5°, $\lambda_{max.}$ 375 mμ (ε 26,590) (Found:

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[12] Inhoffen, Bohlmann, Bartram, Rummert, and Pommer, *Annalen*, 1950, **570**, 54; Inhoffen and Leibner, *ibid.*, 1951, **575**, 105; Ahmad and Weedon, *J.*, 1953, 2126.

[13] Semmler and Becker, *Ber.*, 1913, **46**, 1816; Ruzicka and van Veen, *Annalen*, 1929, **468**, 143; Booker, Evans, and Gillam, *J.*, 1940, 1453; Eschenmoser and Schinz, *Helv. Chim. Acta*, 1950, **33**, 171.

C, 56·4; H, 5·6. Calc. for $C_{15}H_{18}N_4O_4$: C, 56·6; H, 5·6%) [Lewis[3] records m. p. 136°, $\lambda_{max.}$ 376 mμ (ε 29,300); Birch[3] gives m. p. 135—136°]. It gave also *trans*-(±)-cryptol 3,5-dinitrobenzoate, plates, m. p. 108° from methanol (Found: C, 57·3; H, 5·3. Calc. for $C_{16}H_{18}N_2O_6$: C, 57·5; H, 5·4%) (Gillespie and Macbeth[1] record m. p. 108°), and 4-isopropyl-cyclohexanone, b. p. 214—215°/760 mm. [semicarbazone, m. p. 189—190° (Cahn *et al.*[2] give m. p. 188—189°)].

Diethyl 2,6-*Dimethylheptane*-1,1-*dicarboxylate*.—Ethyl sodiomalonate (from sodium, 7·7 g., alcohol, 130 c.c., and ethyl malonate, 53·3 g.) was refluxed with 1,5-dimethylhexyl iodide[14] (80 g.) on the steam-bath for 14 hr. The *product* (71 g.) had b. p. 140—142°/11 mm. (Found: C, 66·0; H, 10·3. $C_{15}H_{28}O_4$ requires C, 66·1; H, 10·2%).

Diethyl 6,10-*Dimethyl*-2-*oxoundecane*-5,5-*dicarboxylate* (VI; R = $[CH_2]_3{\cdot}Pr^i$).—The preceding ester (40·8 g.) was mixed with a solution from sodium (3·4 g.) in absolute alcohol (55 c.c.) and allowed to condense with 4-diethylaminobutan-2-one methiodide[8] (ketone, 21·5 g.; methyl iodide, 11 c.c.) in the usual way. The *keto-ester* (39 g.) was isolated in the usual way and had b. p. 174—175°/7 mm. (Found: C, 66·4; H, 9·8. $C_{19}H_{34}O_5$ requires C, 66·6; H, 9·9%). It did not give a semicarbazone.

Ethyl 6,10-*Dimethyl*-2-*oxoundecane*-5-*carboxylate*.—The preceding diester (36 g.) was refluxed with potassium hydroxide (17 g.), water (17 c.c.), and alcohol (75 c.c.) for 1 hr. The resulting crude dicarboxylic acid was dried in an evacuated desiccator and then heated at 140—145° until no more carbon dioxide was evolved (3 hr.). The residue (31·5 g.) was esterified with ethanolic hydrogen chloride (67 c.c.), giving *ethyl* 6,10-*dimethyl*-2-*oxoundecane*-5-*carboxylate* (16 g.), b. p. 140—142°/5 mm. (Found: C, 71·0; H, 11·0. $C_{16}H_{30}O_3$ requires C, 71·1; H, 11·1%). Attempts to prepare a semicarbazone under the usual condition failed. This keto-ester (16·7 g.) was refluxed with a solution from sodium (1·5 g.) in absolute alcohol (40 c.c.) on the water-bath for 20 hr. The excess of alcohol was evaporated and, after cooling, the alkaline solution was acidified with dilute hydrochloric acid. The viscous oil which separated was collected in ether. The ethereal solution was washed with water, dried (Na_2SO_4), and evaporated. The cyclic diketone (III; R = $[CH_2]_3{\cdot}Pr^i$) (12·8 g.), which showed no tendency to solidify, was not further purified. It gave a violet colour with alcoholic ferric chloride.

3-*Chloro*-6-(1,5-*dimethylhexyl*)*cyclohex*-2-*enone* (IV; R = $[CH_2]_3{\cdot}Pr^i$, R′ = Cl).—A mixture of the above diketone (12·6 g.), dry chloroform (30 c.c.), and phosphorus trichloride[9] (2 c.c.) was refluxed on the water-bath for 3 hr. The solvent was distilled off and the viscous residue shaken with ice-cold water and then extracted with ether. The ethereal solution was washed with dilute aqueous sodium hydroxide and with water, dried ($MgSO_4$), and distilled, giving the *chloride* (6 g.), b. p. 128°/3 mm. (Found: C, 69·1; H, 9·6. $C_{14}H_{23}ClO$ requires C, 69·2; H, 9·4%).

2-(1,5-*Dimethylhexyl*)*cyclohexanone*.—The preceding chloro-compound (5·1 g.), gum arabic (0·1 g.), water (5 c.c.), palladium chloride (0·1 g.), and alcohol (25 c.c.) were shaken in hydrogen until the theoretical amount of hydrogen (2 mol.) was absorbed. The saturated *ketone* (4·8 g.) had b. p. 115—116°/5 mm. (Found: C, 80·2; H, 12·1. $C_{14}H_{26}O$ requires C, 80·0; H, 12·3%). The *semicarbazone* had m. p. 170° (from alcohol) (Found: C, 67·5; H, 10·6. $C_{15}H_{29}N_3O$ requires C, 67·4; H, 10·8%). The 2,4-*dinitrophenylhydrazone* separated from light petroleum (b. p. 40—60°) and had m. p. 120—121° (Found: C, 61·7; H, 7·8. $C_{20}H_{30}N_4O_4$ requires C, 61·5; H, 7·6%).

6-(1,5-*Dimethylhexyl*)-3-*isobutoxycyclohex*-2-*enone* (IV; R = $[CH_2]_3{\cdot}Pr^i$, R′ = OBu^i).—The corresponding diketone (34 g.), isobutyl alcohol (30 c.c.), toluene-*p*-sulphonic acid (0·6 g.), and benzene (114 c.c.) gave enol *isobutyl ether* (28·9 g.), b. p. 165—169°/5 mm. (Found: C, 76·9; H, 11·4. $C_{18}H_{32}O_2$ requires C, 77·1; H, 11·4%).

4-(1,2-*Dimethylhexyl*)*cyclohex*-2-*enone* (V; R = $[CH_2]_3{\cdot}Pr^i$).—The preceding enol isobutyl ether (19 g.) was reduced with lithium aluminium hydride (2·8 g.) under ether (148 c.c.). 4-(1,2-*Dimethylhexyl*)*cyclohex*-2-*enone* (8 g.), b. p. 128—130°/3 mm., had a faint characteristic smell and $\lambda_{max.}$ 228 and 316 mμ (log ε 4·066, 1·603) (Found: C, 81·0; H, 11·3. $C_{14}H_{24}O$ requires C, 80·8; H, 11·5%). The 2,4-*dinitrophenylhydrazone* formed orange red prisms, m. p. 114° (from alcohol), $\lambda_{max.}$ 375 mμ (ε 25, 950) (Found: C, 61·9; H, 7·1. $C_{20}H_{28}N_4O_4$ requires C, 61·8; H, 7·2%).

4-(1,2-*Dimethylhexyl*)*cyclohexanone*.—The foregoing unsaturated ketone (4·1 g.) was hydrogenated over colloidal palladium, giving the saturated *analogue* (2·65 g.), b. p. 122—124°/5 mm.

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[14] Clarke, *J. Amer. Chem. Soc.*, 1909, **31**, 111; Peak and Robinson, *J.*, 1937, 1589.

(Found: C, 80·2; H, 12·1. $C_{14}H_{26}O$ requires C, 80·0; H, 12·3%) [*semicarbazone*, plates (from alcohol), m. p. 155° (Found: C, 67·5; H, 10·6. $C_{15}H_{29}N_3O$ requires C, 67·4; H, 10·8%); 2,4-*dinitrophenylhydrazone*, m. p. 72° after two crystallisations from light petroleum (b. p. 40—60°) (Found: C, 61·7; H, 7·6. $C_{20}H_{30}N_4O_4$ requires C, 61·5; H, 7·6%)].

Ethyl 1,5-*Dimethylhex*-4-*enylmalonate*.—Ethyl sodiomalonate (ethyl malonate, 72 g.; sodium, 9·8 g.; absolute alcohol, 171 c.c.), 1,5-dimethylhex-4-enyl bromide [15] (81·5 g.), and sodium iodide (2 g.) were refluxed for 12 hr. The *product* (87 g.), worked up in the usual way, had b. p. 137—138°/7 mm. (Found: C, 66·5; H, 9·7. $C_{15}H_{26}O_4$ requires C, 66·6; H, 9·6%).

Diethyl 6,10-*Dimethyl*-2-*oxoundec*-9-*ene*-5,5-*dicarboxylate* (VI; R = $CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2$).—The preceding malonate (87 g.) with sodium (7·4 g.) in alcohol (130 c.c.) was allowed to react with diethylaminobutanone methiodide (ketone, 46·1 g.; methyl iodide, 23 c.c.) under the standard conditions,[6] to give *diethyl* 6,10-*dimethyl*-2-*oxoundec*-9-*ene*-5,5-*dicarboxylate* (82·3 g.), b. p. 178—180°/5 mm. (Found: C, 67·1; H, 9·5. $C_{19}H_{32}O_5$ requires C, 67·0; H, 9·4%).

6,10-*Dimethyl*-2-*oxoundec*-9-*ene*-5-*carboxylic Acid* (VII; R = $CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2$, R′ = H).—The foregoing ester (80 g.) was hydrolysed with potassium hydroxide (32 g.) in water (15 c.c.) and alcohol (340 c.c.) in the usual manner. The resulting dicarboxylic acid was heated at 130—140° until evolution of carbon dioxide ceased (3—4 hr.). The residue (65·8 g.) could be distilled in small portions without decomposition, giving 6,10-*dimethyl*-2-*oxoundec*-9-*ene*-5-*carboxylic acid*, b. p. 180—182°/3 mm. (Found: C, 70·2; H, 9·9. $C_{14}H_{24}O_3$ requires C, 70·0; H, 10·0%). The acid gave a semicarbazone rather tardily which, however, could not be obtained pure. The *ethyl ester*, prepared in ethanolic hydrogen chloride, was an oil, b. p. 150—155°/5 mm. (Found: C, 71·5; H, 10·3. $C_{16}H_{28}O_3$ requires C, 71·6; H, 10·4%), that in boiling alcoholic sodium ethoxide readily yielded the dione (III; R = $CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2$), which could not be distilled without decomposition.

3-*Chloro*-6-*methylheptenylcyclohex*-2-*enone* (IV; R = $CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2$, R = Cl).—This *chloride* was prepared by the action of phosphorus trichloride (1·6 c.c.) on the last-mentioned dione (9·8 g.) in chloroform (24 c.c.) in the usual way.[9] It (4 g.) had b. p. 144—145°/4 mm. (Found: C, 69·7; H, 8·9. $C_{14}H_{21}ClO$ requires C, 69·8; H, 8·7%). On hydrogenation over colloidal palladium it gave 2-(1,5-dimethylethylhexyl)cyclohexanone, b. p. 108—110°/3 mm. (Found: C, 80·1; H, 12·4%) (semicarbazone, m. p. 170°; 2,4-dinitrophenylhydrazone, m. p. 120—121°), identical with the ketone described above.

6-(1,5-*Dimethylhex*-4-*enyl*)-3-*isobutoxycyclohex*-2-*enone* (IV; R = $CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2$, R′ = OBu^i).—This *ether* was prepared from the dione (III; R = $CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2$) (14·1 g.), isobutyl alcohol (11 c.c.), benzene (48 c.c.), and toluene-*p*-sulphonic acid (0·5 g.) in the usual way.[7] It was a liquid (9·6 g.), b. p. 175—178°/4 mm. (Found: C, 78·1; H, 10·8. $C_{18}H_{30}O_2$ requires C, 77·7; H, 10·8%).

(1,5-*Dimethylhex*-4-*enyl*)*cyclohex*-2-*enone* (V; R = $CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2$).—The preceding compound (9·6 g.) was reduced with lithium aluminium hydride (1 g.) in dry ether (100 c.c.), giving (1,5-dimethylhex-4-enyl)cyclohex-2-enone (5·4 g.), b. p. 145°/4 mm., $\lambda_{max.}$ 226 and 318 mμ (log ε 3·901, 1·437) (Found: C, 81·4; H, 10·7. Calc. for $C_{14}H_{22}O$: C, 81·5; H, 10·5%). Mukherji and Bhattacharyya [10] record b. p. 148—152°/4 mm., $\lambda_{max.}$ 225 and 285 mμ (log ε 3·76, 2·48). The 2,4-*dinitrophenylhydrazone*, prepared in poor yield, on recrystallisation from methyl alcohol, had m. p. 118°, $\lambda_{max.}$ 375 mμ (ε 23,900) (Found: C, 62·0; H, 6·8. $C_{20}H_{26}N_4O_4$ requires C, 62·1; H, 6·7%). The unsaturated ketone, on hydrogenation over colloidal palladium, gave an excellent yield of the saturated ketone, b. p. 120—121°/4 mm., described above (Found: C, 70·9; H, 12·2%). Its identity was established by the preparation of a semicarbazone, m. p. and mixed m. p. 155°, and a 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 71—72°.

4-(1,5-*Dimethylhexyl*)-1-*methylcyclohex*-2-*enol* (VIII; R = $[CH_2]_3{\cdot}Pr^i$).—Reaction of methylmagnesium iodide (magnesium, 2·2 g.; methyl iodide, 6·7 c.c.; ether, 100 c.c.) on the ketone (V; R = $CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe_2$) (15 g.) was carried out as in the case of cryptone described in the literature.[11] The resulting tertiary *alcohol* (VIII; R = $CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe_2$) (8 g.) had b. p. 140°/3 mm. (Found: C, 80·1; H, 12·6. $C_{15}H_{28}O$ requires C, 80·3; H, 12·5%). Some ketone (6 g.) was recovered.

5-(1,5-*Dimethylhexyl*)-2-*methylcyclohexa*-1,3-*diene* (IX; R = $[CH_2]_3{\cdot}Pr^i$).—After several trials the following method [12] of dehydration was found satisfactory. The preceding alcohol

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[15] Doeuvre, *Bull. Soc. chim. France*, 1929, **45**, 352.

(6·5 g.), dry pyridine (25 c.c.), and toluene (25 c.c.) were cooled in ice, and phosphorus oxychloride (7 c.c.) in toluene (25 c.c.) was gradually introduced, with shaking. The mixture was kept at 85—95° for 30 min., then refluxed for 2 hr. After cooling, ice and hydrochloric acid were added, the toluene layer was separated, and the aqueous solution was extracted with ether. The combined extracts were washed with water, dried ($MgSO_4$), and distilled, giving fractions (1), b. p. 109—110°/3 mm. (3·5 g.), and (2) b. p. 130—135°/3 mm. (2·2 g.). Fraction (1), on redistillation over sodium, gave the cyclo*hexadiene*, b. p. 108°/3 mm., n_D^{36} 1·4692 (Found: C, 87·4; H, 12·3. $C_{15}H_{26}$ requires C, 87·4; H, 12·3%). Fraction (2), which probably consisted of the unchanged alcohol, was not examined.

4-(1,5-*Dimethylhex*-4-*enyl*)-1-*methylcyclohex*-2-*enol* (VIII; R = $CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2$).—A solution of the ketone (V; R = $CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2$) (11 g.) in ether (15 c.c.) was allowed to react with methylmagnesium iodide (magnesium, 1·5 g.; dry ether, 60 c.c.; methyl iodide, 4·5 c.c.), giving the unsaturated alcohol (6 g.), b. p. 153°/3 mm. (lit.,[10] 133—135°/5 mm.) (Found: C, 81·1; H, 11·5. Calc. for $C_{15}H_{26}O$: C, 81·0; H, 11·7%). The reported high yield of the alcohol could not be realised.

5-(1,5-*Dimethylhex*-4-*enyl*)-2-*methylcyclohexa*-2,4-*diene* (IX; R = $CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2$).—In our hands the method of Mukherji and Bhattacharyya [10] proved unsuccessful. Dehydration, however, proceeded satisfactorily under the conditions described above. The product was worked up, in the usual way, and on distillation gave fraction (1), b. p. 115°/3 mm. (3 g.), and (2) b. p. 155°/3 mm. (2·3 g.). Fraction (1), on redistillation over sodium, gave a colourless oil (2·5 g.) having a characteristic sweet smell reminiscent of zingiberene and b. p. 114°/3 mm., n_D^{36} 1·4521, $\lambda_{max.}$ 260 and 232 mμ (log ε 3·013, 3·322) (Found: C, 88·1; H, 11·8. Calc. for $C_{15}H_{24}$: C, 88·2; H, 11·8%). The physical properties are very close to those in the literature.[13] Fraction (2) probably consisted of the unchanged alcohol and on further dehydration yielded the unsaturated hydrocarbon (1·2 g.), b. p. 115°/3 mm.

The ultraviolet absorption spectra were measured for solutions in purified ethanol with a Beckman spectrophotometer, model DU, and we thank Dr. (Miss) K. Rohatgi for valuable help, and Ciba Pharma Ltd. for grants.

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