444. *Terpene Compounds. Part XIII.* Synthesis of the Isomeric* 1,5-*Dimethylhexylcyclohexanones.*

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Isomeric 1,5-dimethylhexylcyclohexanones have been synthesised for comparison with ketones obtained in previous work.

WORK described in Part XII of this series * necessitated preparation of 2- and 4-(1,5-dimethylhexyl)cyclohexanone by unambiguous methods. Comparatively few monocyclic ketones containing this side chain are known.[1] The present paper deals with the synthesis of the three monalkylcyclohexanones.

2-(1,5-*Dimethylhexyl*)*cyclohexanone*.—Ethyl sodio(1,5-dimethylhexyl)malonate was condensed with trimethylene chlorobromide to form the chloro-ester (I), which on treatment with ethyl sodiomalonate afforded the tricarboxylic ester (II) in satisfactory yield. The latter on hydrolysis and decarboxylation gave the substituted pimelic acid (III), and this

$$\mathrm{CHMe_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}C(CO_2Et)_2{\cdot}[CH_2]_3{\cdot}Cl} \quad \text{(I)}$$

$$\mathrm{CHMe_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}C(CO_2Et)_2{\cdot}[CH_2]_3{\cdot}CH(CO_2Et)_2} \quad \text{(II)}$$

$$\mathrm{CHMe_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}CH(CO_2H){\cdot}[CH_2]_3{\cdot}CH_2{\cdot}CO_2H} \quad \text{(III)}$$

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* Part XII, preceding paper.

[1] Rydon, *J.*, **1939**, 1544.

on pyrolysis in presence of a little barium hydroxide yielded 2-(1,5-dimethylhexyl)cyclohexanone, identical with that described in Part XII. Attempts to prepare the acid (III) by alkylation of ethyl 2-oxocyclohexanecarboxylate failed.

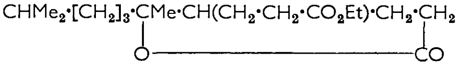
4-(1,5-*Dimethylhexyl*)*cyclohexanone*.—Ethyl 7-methyl-3-oxo-octanoate (IV) was prepared from 6-methylheptanone with ethyl carbonate and sodium hydride under the usual conditions.[2] As in Perkin and Simonsen's work [3] this was condensed with ethyl β-chloropropionate in the presence of sodium ethoxide to give an ester (V) in good yield. The latter with ethyl β-chloropropionate and sodium ethoxide gave the triester (VI) in moderate yield, and thence acid hydrolysis and decarboxylation, followed by esterification, furnished the ketonic ester (VII). The action of methylmagnesium iodide on the latter afforded the lactonic ester (VIII) in poor yield. This could not be converted into the desired pimelic acid derivative (IX) which was, however, prepared as follows: 4,8-Dimethylnonanoic acid, prepared from tetrahydrogeraniol [4] by a known method,[5] was brominated [6] in the presence of red phosphorus and then esterified, giving the bromo-ester (X) in an excellent yield. Jocelyn and Polgar [7] were unable to dehydrobrominate the corresponding methyl ester (as X). In our experience too, this proved extremely troublesome and the difficulty was eventually surmounted by the use of modified conditions [8] under which the desired unsaturated ester (XI) could be isolated in moderate yield. The latter reacted with ethyl malonate in the presence of a minute amount of sodium ethoxide [8] giving an ester (XII) which was hydrolysed to the crystalline dicarboxylic acid (XIII; R = H). The diethyl ester (XIII; R = Et) was reduced with lithium aluminium hydride [10] to the diol (XIV; R = OH) which was converted by way of the corresponding dibromide and dicyanide into the acid (IX), and this was pyrolysed to a ketone, indistinguishable from 4-(1,5-dimethylhexyl)cyclohexanone described in Part XII.

$$\mathrm{CHMe_2{\cdot}[CH_2]_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et} \quad \text{(IV)}$$

$$\mathrm{CHMe_2{\cdot}[CH_2]_3{\cdot}CO{\cdot}CH(CO_2Et){\cdot}[CH_2]_2{\cdot}CO_2Et} \quad \text{(V)}$$

$$\mathrm{CHMe_2{\cdot}[CH_2]_3{\cdot}CO{\cdot}C(CO_2Et)(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2} \quad \text{(VI)}$$

$$\mathrm{CHMe_2{\cdot}[CH_2]_3{\cdot}CO{\cdot}CH(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2} \quad \text{(VII)}$$



$$\begin{array}{l}\mathrm{CHMe_2{\cdot}[CH_2]_3{\cdot}CMe{\cdot}CH(CH_2{\cdot}CH_2{\cdot}CO_2Et){\cdot}CH_2{\cdot}CH_2}\\ \qquad\qquad\quad \mathrm{O}\text{————————}\mathrm{CO}\end{array} \quad \text{(VIII)}$$

$$\mathrm{CHMe_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}CH(CH_2{\cdot}CH_2{\cdot}CO_2H)_2} \quad \text{(IX)}$$

$$\mathrm{CHMe_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2Et} \quad \text{(X)}$$

$$\mathrm{CHMe_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}CH{:}CH{\cdot}CO_2Et} \quad \text{(XI)}$$

$$\mathrm{CHMe_2{\cdot}[CH_2]_3{\cdot}CHMe_2{\cdot}CH(CH_2{\cdot}CO_2Et){\cdot}CH(CO_2Et)_2} \quad \text{(XII)}$$

$$\mathrm{CHMe_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}CH(CH_2{\cdot}CO_2R)_2} \quad \text{(XIII)}$$

$$\mathrm{CHMe_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}CH(CH_2{\cdot}CH_2R)_2} \quad \text{(XIV)}$$

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[2] Salway and La Forge, *J. Amer. Chem. Soc.*, 1947, **69**, 2677; Green and La Forge, *ibid.*, 1948, **70**, 2287; Swamer and Hauser, *ibid.*, 1950, **72**, 1352; Crombie and Harper, *J.*, 1950, 3552.

[3] Perkin and Simonsen, *J.*, 1907, **91**, 1741.

[4] Willstätter and Mayer, *Ber.*, 1908, **41**, 1479; Natelson, Gottfried, and Komblau, *J. Amer. Chem. Soc.*, 1942, **64**, 1484; Ishizaka, *Ber.*, 1914, **47**, 2454; Adams and Garvey, *J. Amer. Chem. Soc.*, 1926, **48**, 477.

[5] von Braun and Kaiser, *Ber.*, 1923, **56**, 2270.

[6] Cf. Zelinsky, *Ber.*, 1887, **20**, 2026; Perkin, *J.*, 1896, **69**, 1471; Bentley and Perkin, *J.*, 1898, **73**, 49.

[7] Jocelyn and Polgar, *J.*, 1953, 133.

[8] Crossley and Le Sueur, *J.*, 1899, **75**, 181; 1900, **77**, 53; Cason and Allen, *J. Biol. Chem.*, 1953, **205**, 449; Cason, *J. Org. Chem.*, 1953, 842, 850.

[9] Michael and Ross, *J. Amer. Chem. Soc.*, 1930, **52**, 4598; 1931, **53**, 1150.

[10] Gaylord, " Reduction with Complex Metal Hydrides," Interscience Publ., Inc., New York, 1956, p. 415; also, Rabjohn, Hopkins, and Nagler, *J. Amer. Chem. Soc.*, 1952, **74**, 3215; Reid, *J. Org. Chem.*, 1953, **18**, 662.

3-(1,5-*Dimethylhexyl*)*cyclohexanone*.—Ethyl acetoacetate was alkylated with isohexyl iodide; the product, on methylation and hydrolysis, gave the ketone (XV) in good yield. This readily condensed with formaldehyde and diethylamine hydrochloride, to give the Mannich base[11] (XVI), the methiodide of which with ethyl sodioacetoacetate gave[12] a product, whose acid hydrolysis furnished 3-(1,5-dimethylhexyl)cyclohex-2-enone in excellent yield. Hydrogenation over colloidal palladium then afforded the cyclohexanone. As an additional control on the constitution of the latter it was also prepared by conventional methods from the substituted glutaric acid (XIII; R = H).

$$\mathrm{CHMe_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}COMe} \quad \text{(XV)}$$

$$\mathrm{CHMe_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2} \quad \text{(XVI)}$$

EXPERIMENTAL

Diethyl 1-*Chloro*-5,9-*dimethyldecane*-4,4-*dicarboxylate* (I).—Diethyl sodio-(1,5-dimethylcyclohexyl)malonate was prepared from powdered sodium (2·9 g.), toluene (125 c.c.), and diethyl 1,5-dimethylhexylmalonate (34 g.), at first at the room temperature and then for a short time at the b. p. Trimethylene chloride bromide[13] (20 g.) was then added and the whole heated at the b. p. for 10 hr. The *ester* (I) (23 g.), which was formed, had b. p. 162—164°/5 mm. (Found: C, 61·7; H, 9·5. $C_{18}H_{33}ClO_4$ requires C, 62·0; H, 9·4%).

Tetraethyl 6,10-*Dimethylundecane*-1,1,5,5-*tetracarboxylate* (II).—The chloro-ester (I) (23 g.) was heated with ethyl sodiomalonate (ethyl malonate, 12 c.c.; sodium, 1·6 g.; absolute alcohol, 25 c.c.) for 12 hr. The *tetraethyl ester* (II) (11·5 g.) had b. p. 212°/5 mm. (Found: C, 63·6; H, 9·1. $C_{25}H_{44}O_8$ requires C, 63·5; H, 9·3%).

This ester (10 g.), potassium hydroxide (8 g.), water (8 c.c.), and alcohol (80 c.c.) were refluxed for 1 hr. The excess of alcohol was removed on the steam-bath, and the residual solution acidified and extracted with ether. The ethereal solution was washed with water, dried, and evaporated. The residual oil (7·5 g.) was heated at 145—150° until evolution of carbon dioxide ceased (3 hr.). The 1,5-*dicarboxylic acid* (III) (5 g.) had b. p. 199—200°/5 mm. (Found: C, 66·0; H, 10·5. $C_{15}H_{28}O_4$ requires C, 66·1; H, 10·3%).

2-(1,5-*Dimethylhexyl*)*cyclohexanone*.—The preceding acid (4 g.) was intimately mixed with powdered barium hydroxide (0·8 g.) and slowly distilled at atmospheric pressure from an air-bath at 350—355°. The distillate was collected in ether, washed, dried (K_2CO_3), and distilled, giving 2-(1,5-dimethylhexyl)cyclohexanone (1·5 g.), b. p. 115—116°/5 mm. (Found: C, 80·1; H, 12·4. Calc. for $C_{14}H_{26}O$: C, 80·0; H, 12·3%) [semicarbazone, m. p. and mixed m. p. 170° (Found: C, 67·5; H, 10·6. Calc. for $C_{15}H_{29}N_3O$: C, 67·4; H, 10·8%); 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 120—121° (Found: C, 61·6; H, 7·4. Calc. for $C_{20}H_{30}N_4O_4$: C, 61·6; H, 7·7%)].

Ethyl 7-*Methyl*-3-*oxo-octanoate* (IV).—6-Methylheptanone (70 g.) in ether (70 c.c.) was added dropwise with stirring to a refluxing suspension of powdered sodium hydride[2] (26 g.), ether (200 c.c.), and ethyl carbonate (150 g.) in 3·5 hr., and stirring and refluxing were continued for a further 2 hr. The product was cooled, the excess of sodium hydride decomposed with absolute alcohol (5 c.c.), and the mixture poured into an excess of ice-cold dilute hydrochloric acid. *Ethyl* 7-*methyl*-3-*oxo-octanoate* (IV) (55 g.), isolated in the usual way, had b. p. 105—107°/5 mm. (Found: C, 65·9; H, 9·8. $C_{11}H_{20}O_3$ requires C, 66·0; H, 10·0%). It gave an intense violet colour with alcoholic ferric chloride.

Ethyl 4-*Ethoxycarbonyl*-9-*methyl*-5-*oxodecanoate* (V).—To a cooled solution of sodium (6·3 g.), in alcohol (110 c.c.), ethyl 7-methyl-3-oxo-octanoate (IV) (55 g.) was added. The resulting solid sodio-derivative was mixed with sodium iodide (1 g.); after cooling, ethyl β-chloropropionate (37·5 g.) was slowly introduced and the mixture heated for 3 hr. on the steam-bath. *Ethyl* 4-*ethoxycarbonyl*-9-*methyl*-5-*oxodecanoate* (V) (59·5 g.) had b. p. 160—162°/3 mm. (Found: C, 64·1; H, 9·5. $C_{16}H_{28}O_5$ requires C, 64·0; H, 9·3%). It gave a deep violet colour with ferric chloride. A higher fraction (10·5 g.), b. p. 190—195°/3 mm., was also obtained (see below).

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[11] Mannich, *Arch. Pharm.*, 1917, **255**, 251; and other publications.

[12] Cf. du Feu, McQuillin, and Robinson, *J.*, 1937, 53.

[13] Hultman, Davis, and Clarke, *J. Amer. Chem. Soc.*, 1921, **43**, 396; Cloke, Anderson, Lachmann, and Smith, *ibid.*, 1931, **53**, 2794.

Ethyl 4-*Ethoxycarbonyl*-4-2′-*ethoxycarbonylethyl*-9-*methyl*-5-*oxodecanoate* (VI).—A solution from sodium (4·6 g.) in alcohol (80 c.c.) was cooled. To it were added successively the ester (V) (60 g.), sodium iodide (1 g.), and ethyl β-chloropropionate (28 g.), and the mixture was refluxed on the steam-bath for 6 hr. The *keto-ester* (VI) (60·5 g.) had b. p. 190—191°/3 mm. (Found: C, 63·1; H, 8·8. $C_{21}H_{36}O_7$ requires C, 63·0; H, 9·0%) and was identical with the high-boiling fraction described above. It gave no colour with ferric chloride.

Ethyl 4-2′-*Ethoxycarbonylethyl*-9-*methyl*-5-*oxodecanoate* (VII).—The keto-ester (VI) (70·5 g.) and hydrochloric acid (180 c.c.) were refluxed for 30 hr. The solution was evaporated and the residue (47·9 g.) was esterified, to give the *diethyl ester* (VII) (43 g.), b. p. 185—187°/7 mm. (Found: C, 65·9; H, 9·5. $C_{18}H_{32}O_5$ requires C, 65·8; H, 9·7%).

5-*Hydroxy*-4-2′-*ethoxycarbonylethyl*-5,9-*dimethyldecanoic Acid Lactone* (VIII).—The keto-ester (VII) (21 g.) in ether (85 c.c.) was added slowly to an ice-cold solution of methylmagnesium iodide (magnesium, 2·5 g.; ether, 25 c.c.; methyl iodide, 7·2 c.c.). The mixture was kept overnight at room temperature, then decomposed with ice and dilute hydrochloric acid. The *lactone* (VIII) (10·2 g.), isolated as usual, had b. p. 180—185°/4 mm. (Found: C, 68·0; H, 10·0. $C_{17}H_{30}O_4$ requires C, 68·5; H, 10·1%). Attempts to convert it into the acid (IX) were unsuccessful.

Ethyl 2-*Bromo*-4,8-*dimethylnonanoate* (X).—4,8-Dimethylnonanoic acid, b. p. 150°/7 mm. (lit.,[5] b. p. 149—152°/14 mm.,[7] 152°/12 mm.) (45 g.), and red phosphorus (3·2 g.) were heated to 50° and dry bromine (31·2 c.c.) was added during 5—6 hr. The temperature was then raised to 60—70° and heating continued for 5 hr. more.[6] The liquid was cooled in a freezing mixture, and absolute alcohol (50 c.c.) introduced with shaking. Next morning the product was heated on a steam-bath for 2 hr. and after cooling, diluted with water and extracted with ether. The ethereal solution was washed with a dilute solution of sodium hydrogen carbonate and with water, dried ($MgSO_4$), and distilled, giving the *bromo-ester* (X) (54 g.), b. p. 113°/6 mm. (Found: C, 53·4; H, 8·3. $C_{13}H_{25}BrO_2$ requires C, 53·2; H, 8·5%).

Ethyl 4,8-*Dimethylnon*-2-*enoate* (XI).—The preceeding bromo-ester (44 g.) was heated with freshly distilled quinoline [8] (44 g.) to 170°, whereupon a vigorous reaction started. The source of heat was removed, the temperature rising spontaneously to 190°, and when the reaction subsided the mixture was heated at 160—170° for 2·5 hr. After cooling, the dark product was mixed with ice, acidified with hydrochloric acid, and extracted with ether continuously for 20 hr. The ethereal solution was washed with dilute hydrochloric acid, a 10% solution of sodium hydrogen carbonate, and water, dried ($MgSO_4$), and distilled. *Ethyl* 4,8-*dimethylnon*-2-*enoate* (XI) (20 g.) boiled at 95—97°/6 mm. (Found: C, 73·8; H, 11·0. $C_{13}H_{24}O_2$ requires C, 73·6; H, 11·3%).

Diethyl 4-*Ethoxycarbonylmethyl*-3,7-*dimethyloctane*-1,1-*dicarboxylate* (XII).—The foregoing unsaturated ester (20 g.) and ethyl malonate (16 g.) were refluxed with a solution of sodium (0·5 g.) in absolute alcohol [9] (25 c.c.) for 6 hr. The *triethyl ester* (18·5 g.) had b. p. 182—183°/6 mm. (Found: C, 64·4; H, 9·9. $C_{20}H_{36}O_6$ requires C, 64·5; H, 9·7%).

β-(1,5-*Dimethylhexyl*)*glutaric Acid* (XIII; R = H).—The above tricarboxylic ester (XII) (17 g.) was refluxed with concentrated hydrochloric acid (111 c.c.) for 80—90 hr., then evaporated to dryness, and the gummy residue which readily solidified crystallised from light petroleum (b. p. 48—60°), affording the *acid* (XIII; R = H) as prisms, m. p. 62° (Found: C, 63·4; H, 9·9. $C_{13}H_{24}O_4$ requires C, 63·9; H, 9·8%). The *diethyl ester* (XIII; R = Et) had b. p. 157°/5 mm. (Found: C, 68·1; H, 10·4. $C_{17}H_{32}O_4$ requires C, 68·0; H, 10·6%).

3-(1,5-*Dimethylhexyl*)*pentane*-1,5-*diol* (XIV; R = OH) *and Derived Compounds*.—A solution of the diester (XIV; R = Et) (35 g.) in ether (250 c.c.) was added slowly with stirring to lithium aluminium hydride [10] (9 g.) in ether (70 c.c.). The product which solidified was stirred and refluxed for 2 hr., left overnight, and again heated for 4 hr. It was decomposed with ice-cold 15% sulphuric acid, the ethereal layer separated, and the aqueous solution extracted continuously with ether. The combined ethereal extracts were washed with aqueous sodium hydrogen carbonate, then with a saturated solution of sodium chloride, dried ($MgSO_4$), and distilled, giving the *diol* (23 g.), b. p. 90°/6 mm. (Found: C, 72·1; H, 13·0. $C_{13}H_{28}O_2$ requires C, 72·2; H, 12·9%).

Phosphorus tribromide [12] (7 c.c.) in carbon tetrachloride (20 c.c.) was added to the diol (21 g.) in carbon tetrachloride (20 c.c.) at 0°. The *dibromide* (XIV; R = Br) distilled as a colourless oil (20·8 g.), b. p. 150—155°/6 mm. (Found: C, 45·5; H, 7·8. $C_{13}H_{26}Br_2$ requires C, 45·6; H, 7·6%).

The dibromide (20 g.), sodium cyanide (18·7 g.), sodium iodide (3·3 g.), and alcohol (123 c.c.) were refluxed for 35 hr., giving the liquid *dinitrile* (XIV; R = CN) (8 g.) b. p. 190—194°/7 mm. (Found: C, 76·8; H, 11·3. $C_{15}H_{26}N_2$ requires C, 76·9; H, 11·1%).

γ-(1,5-*Dimethylhexyl)pimelic Acid* (IX).—The dinitrile (XIV; R = CN) (5 g.) was refluxed with concentrated hydrochloric acid (50 c.c.) for 20 hr., then evaporated, and the residue was collected in ether. On distillation the required *acid* (IX) (4 g.) had b. p. 212°/2 mm. (Found: C, 66·0; H, 10·4. $C_{15}H_{28}O_4$ requires C, 66·1; H, 10·2%).

4-(1,5-*Dimethylcyclohexyl)cyclohexanone*.—This acid (IX) (3 g.) was mixed with barium hydroxide (1 g.) and distilled slowly from an air-bath at 305—310°. The ketone (1·2 g.) had b. p. 130°/8 mm. (Found: C, 80·1; H, 12·4. Calc. for $C_{14}H_{26}O$: C, 80·0; H, 12·3%) and gave a semicarbazone, m. p. and mixed m. p. 155° (Found: C, 67·5; H, 10·6. Calc. for $C_{15}H_{29}N_3O$: C, 67·4; H, 10·8%), and a 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 72° (Found: C, 61·6; H, 7·4. $C_{20}H_{30}N_4O_4$: C, 61·6; H, 7·7%).

Ethyl 2-*acetyl*-6-*methylheptanoate* had b. p. 105—107°/6 mm. (Found: C, 67·3; H, 10·0. $C_{12}H_{22}O_3$ requires C, 67·2; H, 10·2%). *Ethyl* 2-*acetyl*-2,6-*dimethylheptanoate*, obtained by its methylation, had b. p. 103—104°/5 mm. (Found: C, 68·5; H, 10·3. $C_{13}H_{24}O_3$ requires C, 68·4; H, 10·5%).

3,7-*Dimethyloctan*-2-*one* (XV).—The preceding keto-ester (46 g.), acetic acid (180 c.c.), and concentrated hydrochloric acid (60 c.c.) were refluxed for 30 hr. The *ketone*, isolated (27 g.), had b. p. 67—68°/5 mm. (Found: C, 76·8; H, 13·0. $C_{10}H_{20}O$ requires C, 76·9; H, 12·8%). The *semicarbazone* formed scales, m. p. 95—96°, from alcohol (Found: C, 62·0; H, 10·6. $C_{11}H_{23}N_3O$ requires C, 61·9; H, 10·8%).

1-*Diethylamino*-4,8-*dimethylnonan*-3-*one* (XVI).—A mixture of diethylamine hydrochloride (26·6 g.), the ketone (XV) (26 g.), paraformaldehyde (7·5 g.), absolute alcohol (30 c.c.), and concentrated hydrochloric acid (0·5 c.c.) was refluxed [11] on a water-bath for 4 hr. The excess of alcohol was distilled off at the water-pump and the product diluted with water, and potassium hydroxide (21 g.) in water (26 c.c.) was added. The mixture was cooled in ice and extracted with a large volume of ether. The ethereal extract was washed with a saturated solution of sodium chloride, dried (K_2CO_3), and distilled, giving the *amino-nonanone* (29·1 g.), b. p. 120—123°/5 mm. (Found: C, 74·5; H, 13·0. $C_{15}H_{31}NO$ requires C, 74·6; H, 12·8%). A small fraction (4·5 g.), b. p. 60—68°/5 mm., of unchanged octanone was recovered.

3-(1,5-*Dimethylhexyl)cyclohex*-2-*enone*.—Ethyl acetoacetate (8 c.c.) was added to a solution from sodium (1·4 g.) in absolute alcohol (25 c.c.) and, to the mixture cooled in ice, the methiodide from ketone (XVI) (14·5 g.), dissolved in a little absolute alcohol, was gradually introduced.[12] The mixture was kept in ice for 2 hr., then at room temperature overnight, and was finally heated on the water-bath for 6 hr. The crude product (15 g.), isolated as usual, was refluxed with concentrated hydrochloric acid (30 c.c.) and acetic acid (60 c.c.) for 30 hr., giving the *cyclohex*-2-*enone* (4·1 g.), b. p. 125—126°/4 mm. (Found: C, 80·6; H, 11·6. $C_{14}H_{24}O$ requires C, 80·7; H, 11·5%). The *semicarbazone*, after repeated crystallisation from alcohol, had m. p. 116° (Found: C, 67·7; H, 10·3. $C_{15}H_{27}N_3O$ requires C, 67·9; H, 10·1%).

3-(1,5-*Dimethylhexyl)cyclohexanone*.—A mixture of the above unsaturated ketone (6 g.), palladium chloride (0·1 g.), gum arabic (0·1 g.), water (5 c.c.), and alcohol (10 c.c.) was shaken in hydrogen until the calculated amount of gas (700 c.c.) was absorbed. The *cyclohexanone* (5·1 g.) had b. p. 108°/3 mm. (Found: C, 80·1; H, 12·4. $C_{14}H_{26}O$ requires C, 80·0; H, 12·3%). The *semicarbazone* had m. p. 111—112° (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*, had m. p. 106°[from light petroleum (b. p. 40—60°)] (Found: C, 61·6; H, 7·4. $C_{20}H_{30}N_4O_4$ requires C, 61·6; H, 7·7%). These derivatives did not depress the m. p.s of the corresponding derivatives prepared as follows.

β-(1,5-*Dimethylhexylglutaric anhydride*, obtained by heating the acid (XIII; R = H) with acetic anhydride, had b. p. 209—210°/7 mm. (Found: C, 69·1; H, 9·8. $C_{13}H_{22}O_3$ requires C, 69·0; H, 9·7%).

3-2′-*Hydroxyethyl*-4,8-*dimethylnonanoic Acid Lactone*.—The above anhydride (27 g.) in warm, calcium-dried alcohol (110 c.c.) was added rapidly to sodium (22 g.) at 80°. The temperature was allowed to rise to 135—140° and heating continued for 4 hr. more, alcohol (40 c.c.) being added to dissolve the last traces of sodium. The *lactone*, isolated as usual (17 g.), had b. p. 168—170°/7 mm. (Found: C, 73·7; H, 11·5. $C_{13}H_{24}O_2$ requires C, 73·6; H, 11·3%).

Ethyl 3-2′-*Bromoethyl*-4,8-*dimethylnonanoate*.—A mixture of the preceding lactone (16 g.), phosphorus tribromide (8·4 c.c.) was cooled below 0° and bromine (5 c.c.) was added slowly with shaking. After storage at room temperature the mixture was warmed at 60° for 1 hr., and, after cooling, cautiously mixed with alcohol (60 c.c.). The *bromo-ester* (23 g.) had b. p. 155—160°/7 mm. (Found: C, 56·1; H, 9·2. $C_{15}H_{29}BrO_2$ requires C, 56·0; H, 9·0%).

Triethyl (1,5-*Dimethylhexyl*)*pentane*-1,1,5-*tricarboxylate.*—Ethyl malonate (12 g.) was added to a solution from sodium (1·6 g.) in absolute alcohol (33 c.c.), followed by the bromo-ester (21·4 g.), and the whole was refluxed for 16 hr. The *triethyl ester* (20·8 g.) had b. p. 195—200°/17 mm. (Found: C, 66·6; H, 10·0. $C_{22}H_{40}O_6$ requires C, 66·0; H, 10·0%).

This ester (19 g.) was boiled with potassium hydroxide (6 g.) in water (6 c.c.) and alcohol (20 c.c.) for 1 hr. The product (9 g.), obtained as usual, was heated at 140—150° for 3 hr. and on distillation gave β-(1,5-*dimethylhexyl*)*pimelic acid* (6 g.), b. p. 200°/7 mm. (Found: C, 66·0; H, 10·3. $C_{15}H_{28}O_4$ requires C, 66·1; H, 10·2%). This (5 g.), on ketonisation as described above, gave 3-(1,5-dimethylhexyl)cyclohexanone (2·6 g.), b. p. 116°/7 mm. (Found: C, 80·1; H, 12·5%) [semicarbazone, m. p. and mixed m. p. 111° (Found: C, 67·3; H, 10·6%); 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 105° (Found: C, 61·4; H, 7·8%)].

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