325. *Compounds containing the 2 : 2 : 4-Trimethylhexane Skeleton. Part II.**

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The partial optical resolution of 3 : 5 : 5-trimethylhexanol is described. The (+)-form of the alcohol has been converted into the lævorotatory bromide and into (+)-2 : 2 : 4-trimethylhexane. 3 : 3 : 5-Trimethylhex-1-ene has been brominated by *N*-bromosuccinimide in the presence of benzoyl peroxide. 6-Hydroxy-2 : 2 : 4 : 9 : 11 : 11-hexamethyldodecan-7-one and 2 : 2 : 4 : 9 : 11 : 11-hexamethyldodecane-6 : 7-diol have been synthesised.

The partial optical resolution of 3 : 5 : 5-trimethylhexanol, mentioned in Part I,* has been accomplished by the fractional crystallisation, from acetone, of the brucine salt of the hydrogen phthalate. The (+)-3 : 5 : 5-trimethylhexanol obtained, when heated with hydrobromic–sulphuric acid, gave a lævorotatory bromide, the Grignard compound from which yielded (+)-2 : 2 : 4-trimethylhexane on treatment with aqueous ammonium chloride.

The product of brominating 3 : 5 : 5-trimethylhex-1-ene, $CMe_3·CH_2·CHMe·CH{:}CH_2$, with *N*-bromosuccinimide in carbon tetrachloride solution in presence of benzoyl peroxide is a mixture of isomeric bromo-compounds. It reacts with *cyclo*hexylamine to give two different *cyclo*hexyltrimethylhexenylamines, isolable as the hydrochlorides in the weight ratio 8 : 1. Interaction of the mixture of bromo-compounds with sodiomalonic ester, followed by hydrolysis and decarboxylation, and then by hydrogenation, gave 5 : 7 : 7-trimethyloctanoic acid † (compare Kepner, Winstein, and Young, *J. Amer. Chem. Soc.*, 1949, **71**, 115).

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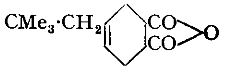
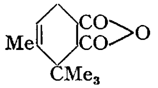
* *J.*, 1951, 2543, is considered as Part I.

† Geneva notation ($CO_2H = 1$) is used for long-chain acids.

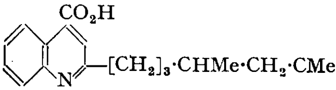
Attempts to eliminate the elements of hydrogen bromide from the monobromo-compounds led to poor yields of a 1 : 3-diolefin. The latter combines with maleic anhydride to give a product which is presumably either (I) or (II).



(I)



(II)



(III)

When heated in xylene solution under nitrogen in the presence of sodium, ethyl 3 : 5 : 5-trimethylhexanoate undergoes the acyloin condensation to give 6-hydroxy-2 : 2 : 4 : 9 : 11 : 11-hexamethyldodecan-7-one, from which 2 : 2 : 4 : 9 : 11 : 11-hexamethyldodecane-6 : 7-diol is obtained by hydrogenation.

6 : 8 : 8-Trimethylnonan-2-one (see Part I, *loc. cit.*) condenses with isatin in the presence of aqueous-alcoholic alkali, and from the product 2-(4 : 6 : 6-trimethylheptyl)quinoline-4-carboxylic acid (III) can be isolated. The constitution of this acid is proved by oxidation to quinoline-2 : 4-dicarboxylic acid. The formation of (III) is in agreement with the conclusions of Buu-Hoï (*J.*, 1946, 795; 1948, 106) that in ketones R·CH$_2$·CO·CH$_3$ the CO·CH$_3$ mainly enters into formation of the quinoline ring if R is an alkyl group larger than methyl.

EXPERIMENTAL

Partial Resolution of 3 : 5 : 5-*Trimethylhexanol.*—A boiling solution of brucine (330 g.) and 3 : 5 : 5-trimethylhexyl hydrogen phthalate (252 g.) in acetone (550 c.c.) gave, when cooled, 141·5 g. of brucine salt. Two recrystallisations of this from the minimum of acetone gave 121 g. of salt with $[\alpha]^{25}_{5461}$ $-25{\cdot}6°$ ($c = 1{\cdot}6$, $l = 2$, in chloroform). Further recrystallisations caused no change in rotation. A solution of the salt (88 g.) in acetone (700 c.c.) was poured into N-hydrochloric acid (3 l.). (+)-Trimethylhexyl hydrogen phthalate (31·5 g.) was obtained, and after recrystallisation from light petroleum (b. p. 40—60°) had m. p. 69—69·5° and $[\alpha]^{25}_{5461}$ +7·7°, +7·6°, and +7·3° (for $c = 3{\cdot}75$, 3·00, and 2·40, respectively, $l = 2$, in chloroform). Hydrolysis of the ester gave (+)-3 : 5 : 5-trimethylhexanol with n^{25}_{D} 1·4303, d^{25} 0·8240, $[\alpha]^{25}_{5461}$ +6·7°. (−)-3 : 5 : 5-Trimethylhexyl bromide, prepared as for the (±)-compound (Part I), had b. p. 84°/21 mm., n^{22}_{D} 1·4528, d^{25} 1·073, $[\alpha]^{25}_{2461}$ −6·76°.

(+)-2 : 2 : 4-*Trimethylhexane.*—The Grignard solution from 17·7 g. of (−)-bromide was treated with aqueous ammonium chloride; the hydrocarbon isolated in the usual manner (40%), had n^{20}_{D} 1·4034, d^{25} 0·711, $[\alpha]^{25}_{5461}$ +15·2°.

Bromo-3 : 5 : 5-*trimethylhex*-1-*enes.*—Pyrolysis of 3 : 5 : 5-trimethylhexyl acetate over glass wool at 500° gave 3 : 5 : 5-trimethylhex-1-ene. A solution of the latter (251 g.), *N*-bromosuccinimide (120 g., 1 mol.), and benzoyl peroxide (1 g.) in carbon tetrachloride (200 c.c.) was stirred and boiled under reflux for 7 hours. By usual methods the bromo-olefin mixture (67·5 g., 49%) was isolated as a pale yellow, lachrymatory liquid, b. p. 46—68°/1·5 mm., n^{25}_{D} 1·4832 (Found : C, 53·4; H, 8·3; Br, 39·5. Calc. for $C_9H_{17}Br$: C, 52·7; H, 8·3; Br, 39·0%).

Interaction of the Bromo-olefin Mixture with cyclo*Hexylamine.*—*cyclo*Hexylamine (45 g.) was added gradually to a solution of the bromo-olefin mixture (30 g.) in 50 c.c. of anhydrous ether at 40°. *cyclo*Hexylamine hydrobromide (28 g.; m. p. 197°) was removed by filtration. The ethereal solution was extracted with water, and excess of concentrated hydrochloric acid was added to the aqueous solution. The colourless precipitate (11 g.) of mixed hydrochlorides, m. p. 162—165° (Found : C, 69·5; H, 11·6; N, 5·6; Cl, 13·3. Calc. for $C_{15}H_{30}NCl$: C, 69·3; H, 11·6; N, 5·4; Cl, 13·7%), was fractionally crystallised from light petroleum (b. p. 80—120°) : 0·9 g. of a *hydrochloride*, m. p. 139—140° (Found : N, 5·25; Cl, 12·7%), and 7·6 g. of a second *hydrochloride*, m. p. 182—183° (Found : N, 5·2; Cl, 13·3%), were isolated. From the second salt excess of aqueous alkali liberated a *base*, b. p. 94°/0·5 mm., n^{24}_{D} 1·4737 (Found : N, 6·2. $C_{15}H_{29}N$ requires N, 6·3%).

Dehydrobromination of the Bromo-olefin Mixture.—(*a*) The bromo-compound (9 g.) was dropped on potassium hydroxide pellets at 150—200°. A distillate (1·5 g.) was obtained which, when heated in benzene with maleic anhydride, and then cooled, gave 0·35 g. of colourless leaflets, m. p. 115° [after being washed with light petroleum (b. p. 40—60°)] (Found : C, 70·2; H, 7·8. $C_{13}H_{18}O_3$ requires C, 70·2; H, 8·1%).

(*b*) The bromo-olefin mixture (24 g.), silver acetate (21 g., 1·1 mol.) and benzene (100 c.c.) were heated under reflux for 6 hours; 20·1 g. (93% yield) of a *nonenyl acetate*, b. p. 54—

56°/1 mm., n_D^{23} 1·4442—1·4460, were obtained (Found : C, 71·5; H, 11·0. $C_{11}H_{20}O_2$ requires C, 71·7; H, 10·9%). Pyrolysis of the acetate (18 g.) over glass wool at 490—510° gave 3·5 g. of liquid, b. p. 124—132°, n_D^{19} 1·4467—1·4508, which yielded 1·1 g. of maleic anhydride adduct, m. p. 113·5—114·5°.

Conversion of the Bromo-olefin Mixture into 5 : 7 : 7-*Trimethyloctanoic Acid.*—To sodium (2·3 g., 1 atom) and ethyl malonate (16 g., 1 mol.) in xylene (60 c.c.) at 30° were added, during 30 minutes, 20·5 g. (1 mol.) of bromo-olefin mixture. After 4 hours at 30°, followed by 3 hours at the b. p., the xylene was distilled off under reduced pressure, and the residue hydrolysed with aqueous potassium hydroxide. This gave an unsaturated acid (10·5 g., 59%), b. p. 123—125°/1 mm., n_D^{21} 1·4548—1·4558. Thereafter normal hydrogenation procedure (ethanol; PtO_2; 3—5 atm. of hydrogen) gave a 40% yield of 5 : 7 : 7-trimethyloctanoic acid, b. p. 98—99°/1 mm., n_D^{25} 1·4361. The *p*-bromophenacyl ester had m. p. 68·5°, undepressed by admixture with an authentic sample.

6-*Hydroxy*-2 : 2 : 4 : 9 : 11 : 11-*hexamethyldodecan*-7-*one.*—To a vigorously stirred mixture of sodium (4·6 g., 2 atoms) and xylene (120 c.c.) in an atmosphere of ntrogen, and at 110°, was added, during 1·5 hours, ethyl 3 : 5 : 5-trimethylhexanoate (18·6 g.). After a further 0·5 hour's heating, the product was worked up in the usual way and gave 6-*hydroxy*-2 : 2 : 4 : 9 : 11 : 11-*hexamethyldodecan*-7-*one* (12 g.), b. p. 125—133°/0·5 mm., n_D^{22} 1·4488 (Found : C, 76·2; H, 12·4. $C_{18}H_{36}O_2$ requires C, 76·0; H, 12·7%).

2 : 2 : 4 : 9 : 11 : 11-*Hexamethyldodecane*-6 : 7-*diol.*—Hydrogenation at 20°/3—5 atm. of the acyloin (36 g.), in ethyl alcohol (100 c.c.), in presence of platinum oxide, gave 2 : 2 : 4 : 9 : 11 : 11-*hexamethyldodecane*-6 : 7-*diol* (29 g., 81% yield), b. p. 122—124°/0·2 mm., n_D^{20} 1·4471 (Found : C, 76·1; H, 12·8. $C_{18}H_{38}O_2$ requires C, 75·5; H, 13·3%).

2-(4 : 6 : 6-*Trimethylheptyl*)*quinoline*-4-*carboxylic Acid.*—A mixture of isatin (4·9 g.), sodium hydroxide (7 g.), 6 : 8 : 8-trimethylnonan-2-one (5·7 g.), water (25 c.c.), and ethyl alcohol (15 c.c.) was heated at 85° for 10 hours. 6N-Hydrochloric acid (50 c.c.) was added and the precipitated 2-(4 : 6 : 6-*trimethylheptyl*)*quinoline*-4-*carboxylic acid* (8·9 g., 85%) was crystallised from 60% aqueous alcohol. The *acid* had m. p. 139·5° (softens) to 142° (Found: C 76·3; H, 8·3; N, 4·3. $C_{20}H_{27}O_2N$ requires C, 76·6; H, 8·6; N, 4·4%).

Oxidation of 2-(4 : 6 : 6-*Trimethylheptyl*)*quinoline*-4-*carboxylic Acid.*—To a solution of the acid (1·5 g.) in a solution of sodium hydroxide (10 g.) in water (45 c.c.) was added, in five portions, a solution of potassium permanganate (5 g.) in water (100 c.c.). After the mixture had been heated at 100° until the oxidation was complete, the solution was filtered and acidified, and then submitted to steam-distillation to remove aliphatic acids. The hot aqueous residual solution was filtered, and deposited on cooling a pale yellow precipitate of quinoline-2 : 4-dicarboxylic acid, m. p. 243° (Found : C, 60·1; H, 3·8. Calc. for $C_{11}H_7O_4N$: C, 60·9; H, 3·2%).

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