566. *Compounds Containing the* 2 : 2 : 4-*Trimethylhexyl Skeleton. Part I.*

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The synthesis of 2 : 2 : 4 : 7-tetramethyloctane and 6-ethyl-2 : 2 : 4-trimethyloctane and of related compounds is described.

Since the asymmetric carbon atom in 3 : 5 : 5-trimethylhexanol, $CMe_3{\cdot}CH_2{\cdot}\overset{*}{C}HMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, is on the one hand attached to a *neo*pentyl group and is on the other in the β-position to a primary alcohol group, this alcohol presents features of considerable interest. It is hoped later to describe the behaviour of the optically active alcohol, but in the present communication we are concerned with a preliminary study of the synthetic uses of the racemic material, supplementary to those reported by Keulmanns, Kwantes, and von Bavel (*Rec. Trav. chim.*, 1948, **67**, 298) and Bruner (*Ind. Eng. Chem.*, 1949, **41**, 2860). The former authors concluded that 3 : 5 : 5-trimethylhexanol, as made by the " oxo " reaction from di*iso*butylene, carbon monoxide, and hydrogen, was free from isomers and this we have confirmed by purifying the alcohol through the hydrogen phthalate : the alcohol obtained was indistinguishable from the commercial material after the latter had been distilled.

The trimethylhexanol is smoothly converted by hot hydrobromic–sulphuric acid into the bromide (compare Bruner, *loc. cit.*), the Grignard reagent from which reacts with acetone to give 2 : 5 : 7 : 7-tetramethyloctan-2-ol. From this alcohol, by dehydration, followed by hydrogenation, 2 : 2 : 4 : 7-tetramethyloctane has been prepared.

3 : 5 : 5-Trimethylhexyl bromide and ethyl sodioacetoacetate give ethyl 3 : 5 : 5-trimethylhexylacetoacetate, convertible in good yield into 6 : 6 : 8-trimethylnonan-2-one and in rather poor yield into 5 : 7 : 7-trimethyloctanoic acid. This acid is alternatively obtainable by reduction of 5 : 7 : 7-trimethyloct-2-enoic acid, the product of heating 3 : 5 : 5-trimethylhexanal with malonic acid and pyridine.

The ethyl ester of 3 : 5 : 5-trimethylhexanoic acid, obtained by oxidising the trimethylhexanol, reacts normally with ethylmagnesium bromide to give 3-ethyl-5 : 7 : 7-trimethyloctan-3-ol, and elimination of water from the latter produces what appears to be a single olefin, which, when catalytically hydrogenated, gives 6-ethyl-2 : 2 : 4-trimethyloctane.

Experiments are in progress on the optical resolution of some of the alcohols and acids.

EXPERIMENTAL.

3 : 3 : 5-*Trimethylhexyl Hydrogen Phthalate.*—A mixture of 3 : 5 : 5-trimethylhexanol (144 g., 1 mole), phthalic anhydride (148 g., 1 mole), and pyridine (79 g., 1 mole) was heated at 100° for 2½ hours. The mixture was poured into excess of dilute hydrochloric acid and the solid collected, ground, and washed with dilute hydrochloric acid. It was dissolved in light petroleum (b. p. 40—60°), and the solution was extracted with water. The solvent was removed and the dried residue was twice crystallised from light petroleum (b. p. 40—60°). The *hydrogen phthalate* had m. p. 52—52·5° (Found: C, 69·3; H, 8·0%; equiv., 292. $C_{17}H_{24}O_4$ requires C, 69·9; H, 8·2%; equiv., 292).

The hydrogen phthalate was hydrolysed in boiling 30% aqueous sodium hydroxide solution, and the product distilled in steam. After separation and distillation a 92% yield was obtained of 3 : 5 : 5-trimethylhexanol, b. p. 192·7°/759 mm. (corr.), n_D^{25} 1·4305 (Found: C, 75·6; H, 13·9. Calc. for $C_9H_{20}O$: C, 75·0; H, 13·9%).

3 : 5 : 5-*Trimethylhexyl Bromide.*—A mixture of trimethylhexanol (576 g., 1 mol.), 48% aqueous hydrobromic acid (1076 c.c., 2·5 mols.) and concentrated sulphuric acid (588 g., 1·5 mols.) was heated for 5 hours at 110°. The bromide layer was dissolved in light petroleum (b. p. 40—60°), and the solution washed with water, concentrated sulphuric acid, water, and finally sodium hydrogen carbonate solution. It was dried azeotropically with benzene and then distilled. The bromide (564 g., 68%) had b. p. 72·5°/12·5 mm., n_D^{25} 1·4516 (Found: C, 52·1; H, 8·6; Br, 38·8. Calc. for $C_9H_{19}Br$: C, 52·2; H, 9·2; Br, 38·7%).

2 : 5 : 7 : 7-*Tetramethyloctan*-2-*ol.*—Magnesium turnings (13·4 g., 1·1 atoms), activated under ether by means of a trace of iodine, reacted with 3 : 5 : 5-trimethylhexyl bromide (104 g., 1 mol.) at the boiling point of the mixture. When no further change occurred, acetone (30 g., 1 mol.) was added gradually at the ordinary temperature. After 15 hours, aqueous ammonium chloride was added and the ethereal layer separated, washed, and dried. Distillation gave 2 : 5 : 7 : 7-*tetramethyloctan*-2-*ol* (69 g., 74%), b. p. 85·5—88°/5 mm., n_D^{25} 1·4360 (Found: C, 77·2; H, 13·9. $C_{12}H_{26}O$ requires C, 77·4; H, 14·0%).

2 : 2 : 4 : 7-*Tetramethyloctane.*—The tetramethyloctanol (60 g.) was heated with naphthalene-2-sulphonic acid (0·6 g.). The olefinic *product* (44 g., 81%) had b. p. 71—76°/17 mm. (Found: C, 85·5; H, 14·3. $C_{12}H_{24}$ requires C, 85·7; H, 14·3%). It was hydrogenated in ethyl alcoholic solution at 3—5 atm. pressure in the presence of Adams's platinum oxide catalyst, the product being extracted with concentrated sulphuric acid at 0° and washed with aqueous sodium hydrogen carbonate and with water. The 2 : 2 : 4 : 7-*tetramethyloctane* had b. p. 184·5—184·9°/758 mm. (corr.), n_D^{25} 1·4163 (Found: C, 84·7; H, 15·1. $C_{12}H_{26}$ requires C, 84·7; H, 15·3%).

3 : 6 : 8 : 8-*Tetramethylnonan*-3-*ol.*—This was obtained from trimethylhexylmagnesium bromide and ethyl methyl ketone in 63% yield; the *alcohol* had b. p. 85—88°/2·8 mm., n_D^{25} 1·4408 (Found: C, 77·8; H, 13·9. $C_{13}H_{28}O$ requires C, 78·0; H, 14·0%).

Ethyl 3 : 5 : 5-*Trimethylhexylacetoacetate.*—To a boiling solution prepared by using sodium (3·4 g., 1 atom), ethyl alcohol (105 c.c.), and ethyl acetoacetate (22 g., 1 mol.) was added, during 3 hours, 3 : 5 : 5-trimethylhexyl bromide (34 g.). After a further 3 hours' boiling, the alcohol was distilled off and the residue extracted with ether. The extract was washed with sodium hydrogen carbonate, dried, and distilled. *Ethyl trimethylhexylacetoacetate* was obtained in 46% yield; it had b. p. 109°/2 mm., n_D^{25} 1·4389 (Found: C, 69·9; H, 11·1. $C_{15}H_{28}O_3$ requires C, 70·3; H, 10·9%).

5 : 7 : 7-*Trimethyloct*-2-*enoic Acid.*—A mixture of 3 : 5 : 5-trimethylhexanal (15·3 g., 1 mol.), malonic acid (12 g., 1 mol.), and pyridine (15 c.c.) was heated at 100° for 2·5 hours. The ice-cooled mixture was acidified with dilute sulphuric acid, and the mixture extracted with ether. The ethereal portion was extracted with aqueous sodium hydrogen carbonate, and the aqueous layer acidified and extracted with ether. Distillation gave 5 : 7 : 7-*trimethyloct*-2-*enoic acid* (8·5 g., 47% yield), b. p. 143—145°/8 mm., n_D^{25} 1·4548 (Found: C, 72·1; H, 10·8. $C_{11}H_{20}O_2$ requires C, 71·7; H, 10·8%).

5 : 7 : 7-*Trimethyloctanoic Acid.*—(*a*) Trimethyloctenoic acid was hydrogenated in 95% ethyl alcohol in the presence of Adams's platinum oxide. The *trimethyloctanoic acid*, obtained in 72% yield, had b. p. 100°/1 mm., n_D^{25} 1·4361 (Found: equiv., 188. $C_{11}H_{22}O_2$ requires equiv., 186). The p-*bromophenacyl* ester had m. p. 69° (Found: Br, 20·7. $C_{19}H_{27}O_3Br$ requires Br, 20·9%).

(*b*) A solution of ethyl trimethylhexylacetoacetate (18·5 g.) and potassium hydroxide (22 g.) in ethyl alcohol (45 c.c.) was boiled for 5 hours under reflux. The product was poured into water, and non-acidic material removed by ether extraction. The aqueous portion was acidified and extracted with ether. Distillation of the extract gave 5 : 7 : 7-trimethyloctanoic acid (yield 24%), b. p. 114°/3 mm., n_D^{25} 1·4362 (Found: equiv., 187). The *p*-bromophenacyl ester had m. p. 69° and was identical with the corresponding product from (*a*).

6 : 8 : 8-*Trimethylnonan*-2-*one.*—Ethyl trimethylhexylacetoacetate (40 g.) was stirred for 30 hours with 5% aqueous sodium hydroxide (400 c.c.). The undissolved material was then extracted with ether, and the aqueous solution acidified with sulphuric acid and distilled in steam. The distillate was extracted with ether, etc. The 6 : 8 : 8-trimethylnonan-2-one (19·5 g., 67% yield) had b. p. 84°/4 mm., n_D^{24} 1·4300 (Found: C, 77·8; H, 12·9. $C_{12}H_{24}O$ requires C, 78·3; H, 13·0%). The *semicarbazone* had m. p. 106° (Found: N, 17·6. $C_{13}H_{27}ON_3$ requires N, 17·4%).

3 : 5 : 5-*Trimethylhexanoic Acid.*—Oxidation of trimethylhexanol with chromic anhydride in aqueous acetic acid gave the hexanoic acid, b. p. 120°/13 mm., n_D^{26} 1·4270 (Found: C, 69·0; H, 11·5. Calc. for $C_9H_{18}O_2$: C, 68·4; H, 11·4%). The *acid chloride* was obtained by using phosphorus pentachloride (yield, 88%); it had b. p. 98°/53 mm., n_D^{22} 1·4350 (Found: C, 61·2; H, 9·6; Cl, 19·9. $C_9H_{17}OCl$ requires

C, 61·2; H, 9·6; Cl, 20·1%). The *ethyl* ester was formed in 84% yield when the acid chloride was added to ethyl alcohol and pyridine. It had b. p. 103°/35 mm., n_D^{25} 1·4177 (Found: C, 70·3; H, 11·7. $C_{11}H_{22}O_2$ requires C, 70·9; H, 11·8%).

3-*Ethyl*-5 : 7 : 7-*trimethyloctan*-3-*ol*.—Ethyl trimethylhexanoate (62 g.) was added to ethereal ethylmagnesium bromide (2·5 mols.) and the product worked up in the usual manner. The alcohol was obtained in 60% yield, and had b. p. 92°/7 mm., n_D^{26} 1·4427 (Found: C, 77·7; H, 13·8. $C_{13}H_{28}O$ requires C, 78·0; H, 14·0%).

6-*Ethyl*-2 : 2 : 4-*trimethyloctane*.—Dehydration of trimethylethyloctanol by distillation with naphthalene-2-sulphonic acid gave an 84% yield of olefin, b. p. 92—93°/27 mm. This was hydrogenated in ethanolic solution at 3—5 atm. (platinum oxide catalyst) whereby 6-*ethyl*-2 : 2 : 4-*trimethyloctane* was obtained; it had b. p. 203·5—203·9°/763 mm. (corr.), n_D^{25} 1·4248 (Found: C, 84·8; H, 15·1. $C_{13}H_{28}$ requires C, 84·8; H, 15·2%).

We acknowledge a grant from the Institute of Petroleum Hydrocarbon Research Panel.

BEDFORD COLLEGE, LONDON. [*Received, June 28th*, 1951.]