

738. *The Synthesis and Reactions of Branched-chain Hydrocarbons. Part II.* Hydrocarbons with Two or More Quaternary Carbon Atoms.*

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2 : 2 : 6 : 6-Tetramethyloctane has been prepared by the reaction of 6-chloro-2 : 2 : 6-trimethyloctane with methylmagnesium iodide. 2 : 2 : 9 : 9-Tetramethyldecane, 3 : 3 : 10 : 10-tetramethyldodecane, and 2 : 2 : 15 : 15-tetramethylhexadecane have been obtained by reaction of the appropriate Grignard reagent with silver bromide; and 2 : 2 : 6 : 10 : 10-pentamethyl- and 2 : 2 : 10 : 10 - tetramethyl - 6 - (4 : 4 - dimethylpentyl)undecane and 3 : 3 : 7 : 11 : 11-pentamethyltridecane by hydrogenation of the corresponding olefins. The structures of these olefins have been established by ozonolysis.

The investigation described in Part I* of this series has been continued with alkyl halides $R \cdot CMe_2 \cdot [CH_2]_x \cdot CH_2Br$ ($R = Me$ or Et ; $x = 2$ or 5), which are readily accessible by the peroxide-catalysed addition of hydrogen bromide to olefins $R \cdot CMe_2 \cdot [CH_2]_{x-1} \cdot CH \cdot CH_2$. Three such bromides were prepared by the technique described by Hickinbottom and Porter (*J. Inst. Petr.*, 1949, **35**, 624), namely: 1-bromo-4 : 4-dimethylpentane, 1-bromo-4 : 4-dimethylhexane, and 1-bromo-7 : 7-dimethyloctane; there was no evidence of the formation of appreciable quantities of the isomeric bromides in these preparations although particular attention was paid to this since Whitmore and Homeyer (U.S.P. 2,151,252) reported that a serious proportion of 2-bromo-4 : 4-dimethylhexane was formed from 4 : 4-dimethylhex-1-ene. That the product obtained in the present work is indeed 1-bromo-4 : 4-dimethylhexane was shown by the following sequence of reactions: alkyl bromide \longrightarrow 4 : 4-dimethylhexan-1-ol \longrightarrow 3 : 3-dimethylpentane-1-carboxylic acid. The identity of 1-bromo-7 : 7-dimethyloctane was established in a similar manner.

The Grignard compounds derived from these bromo-compounds yielded the following alcohols by reaction with suitable ketones: 3 : 7 : 7-trimethyloctan-3-ol; 3 : 7 : 7-trimethylnonan-3-ol; 2 : 2 : 6-trimethylundecan-6-ol; 3 : 10 : 10-trimethylundecan-3-ol; and 2 : 2 : 6-trimethylpentadecan-6-ol.

It was hoped that conversion of these alcohols into the corresponding chloride and then the action of methylmagnesium iodide would provide a convenient route to hydrocarbons with two quaternary carbon atoms. Experience with 6-chloro-2 : 2 : 6-trimethyloctane showed that 2 : 2 : 6 : 6-tetramethyloctane could be prepared in this way, but the yield was poor and

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removal of the associated olefins was tedious and made isolation of the pure hydrocarbon difficult. As this method was unsatisfactory, the reaction of our Grignard reagents with silver bromide (Gardner and Bergstrom, *J. Amer. Chem. Soc.*, 1929, **51**, 3375) was examined: 2 : 2 : 9 : 9-tetramethyldecane, 3 : 3 : 10 : 10-tetramethyldecane, and 2 : 2 : 15 : 15-tetramethyldecane were thus prepared in 53—66% yield.

An alternative route to paraffins with at least two quaternary carbon atoms consists in the hydrogenation of olefins derived from alcohols formed by the reaction of our Grignard compounds with esters of carboxylic acids. From ethyl acetate, 2 : 2 : 6 : 10 : 10-pentamethylundecan-5-ol and 3 : 3 : 7 : 11 : 11-pentamethyltridecan-7-ol were prepared in good yield; 2 : 2 : 10 : 10-tetramethyl-6-(4 : 4-dimethylpentyl)undecan-6-ol was similarly obtained from ethyl 4 : 4-dimethylpentane-1-carboxylate. The dehydration of alcohols having quaternary carbon atoms may result in an alteration in the carbon skeleton to a greater or less extent. It was found that a smooth and satisfactory dehydration could be effected by refluxing them with phthalic anhydride and no evidence of rearrangement during the process could be detected on examination of the products of ozonolysis of the olefins thus formed. This method of dehydration appears to have advantages over those generally used for tertiary alcohols; it avoids the inconveniences of the Tschugaeff technique, whereas the alternative method of refluxing them with acetic anhydride and sodium acetate introduces small amounts of impurities which are difficult to remove (Hickinbottom and Sandrock, unpublished observations).

In our dehydrations it was observed that tertiary alcohols $R_2CMe\cdot OH$ gave only a relatively low proportion of olefins of the type $R_2C\cdot CH_2$; loss of water occurred mainly in the direction of the larger groups.

Hydrogenation of the olefins in presence of Raney nickel at 100°/30—40 atmospheres gave the corresponding paraffins smoothly and in good yield.

EXPERIMENTAL.

(Microanalyses are by Drs. Weiler and Strauss. M. p.s are uncorrected.)

1-Bromo-4 : 4-dimethylpentane was obtained in 85% yield by the addition of hydrogen bromide to 4 : 4-dimethylpent-1-ene in benzene containing approx. 0.2% of ascaridole (Hickinbottom and Porter, *J. Inst. Petr.*, 1949, **35**, 624): it had b. p. 56—57°/19 mm. and n_D^{20} 1.4485. Whitmore and Homeyer (*J. Amer. Chem. Soc.*, 1933, **55**, 4555) give b. p. 70—71°/35 mm., n_D^{20} 1.4484.

1-Bromo-4 : 4-dimethylhexane, prepared similarly from 4 : 4-dimethylhex-1-ene in 67% yield, had b. p. 82.5—84.2°/23 mm., n_D^{20} 1.4579—1.4582 (Found: C, 49.9; H, 8.75; Br, 41.3. Calc. for $C_8H_{17}Br$: C, 49.75; H, 8.85; Br, 41.4%). It was characterised by its mercuribromide, m. p. 97—98° (Marvel, Gauerke, and Hill, *ibid.*, 1925, **47**, 3009). There was no detectable amount of the lower-boiling 2-bromo-4 : 4-dimethylhexane which Whitmore and Homeyer (*loc. cit.*) report as one of the products of the peroxide-catalysed addition of hydrogen bromide to 4 : 4-dimethylhex-1-ene in the absence of a diluent.

1-Bromo-4 : 4-dimethylhexane in ether gives the Grignard compound in an average yield of 77%; aerial oxidation affords 4 : 4-dimethylhexan-1-ol, b. p. 95—98°/21 mm., n_D^{20-1} 1.4351 (68% yield), which gives a *hydrogen 3-nitrophthalate*, m. p. 181° (Found: C, 60.0; H, 6.45; N, 4.45. $C_{16}H_{21}O_6N$ requires C, 59.4; H, 6.55; N, 4.3%). Oxidation of the alcohol by dichromate and aqueous sulphuric acid gave 3 : 3-dimethylpentane-1-carboxylic acid, b. p. 139—140.5°/28 mm., n_D^{20-1} 1.4324 (61% yield) (Found: C, 66.6; H, 11.1. Calc. for $C_8H_{16}O_2$: C, 66.6; H, 11.2%), the *S*-benzylthiuronium salt of which has m. p. 152—153° (Campbell, Carter, and Slater, *J.*, 1947, 1745, give m. p. 150°) (Found: C, 61.4; H, 8.4; N, 9.1; S, 10.3. Calc. for $C_{16}H_{26}O_2N_2S$: C, 61.9; H, 8.4; N, 9.0; S, 10.3%); the *p*-*bromophenacyl* ester has m. p. 68° (Found: C, 56.65; H, 6.3. $C_{18}H_{21}O_3Br$ requires C, 56.3; H, 6.2%).

4 : 4-Dimethylhex-1-ene, used as a starting point for the preparation of 1-bromo-4 : 4-dimethylhexane was prepared in 57% yield by reaction of allyl bromide with *tert.*-amylmagnesium chloride in ether at 12—15° (Whitmore and Homeyer, *loc. cit.*; Liberman and Kazansky, *Compt. rend. Acad. Sci. Russ.*, 1943, **40**, 353).

1-Bromo-7 : 7-dimethyloctane (Found: C, 54.8; H, 9.9; Br, 36.3. $C_{10}H_{21}Br$ requires C, 54.3; H, 9.6; Br, 36.1%) was obtained in 82% yield by the addition of hydrogen bromide to 7 : 7-dimethyloct-1-ene, b. p. 96—100°/13 mm., n_D^{20-1} 1.4549—1.4550. It formed the alkylmagnesium bromide (in 90% yield), which by aerial oxidation gave 7 : 7-dimethyloctan-1-ol (56%), b. p. 103—104°/15 mm., n_D^{15} 1.4384 [*hydrogen 3-nitrophthalate*, m. p. 166° (Found: C, 61.5; H, 7.1; N, 4.4. $C_{18}H_{25}O_6N$ requires C, 61.5; H, 7.2; N, 4.0%)]. Oxidation of the alcohol (5.3 g.) by dichromate and aqueous sulphuric acid gave 6 : 6-dimethylheptane-1-carboxylic acid, b. p. 138—139°/9 mm., n_D^{20} 1.4338 (2.8 g.) (Found: C, 69.5; H, 11.65. $C_{10}H_{20}O_2$ requires C, 69.7; H, 11.7%), which affords a *p*-*phenylphenacyl* ester, m. p. 80° (Found: C, 78.1; H, 8.2. $C_{24}H_{30}O_3$ requires C, 78.6; H, 8.25%), and a *p*-*bromophenacyl* ester, m. p. 82°.

7 : 7-Dimethyloct-1-ene, obtained in 80% yield by the reaction of allyl bromide (88 g.) with the Grignard compound from 1-bromo-4 : 4-dimethylpentane (161 g.), had b. p. 152—152.5°, n_D^{20} 1.4183 (Found: C, 85.8; H, 14.0. $C_{10}H_{20}$ requires C, 85.6; H, 14.4%). Ozonolysis in chloroform gave formaldehyde (dimedone derivative, m. p. and mixed m. p. 190°) and 5 : 5-dimethylhexane-1-carboxylic

acid, b. p. 128—130°/11 mm., n_D^{20} 1.4300 (*p*-phenylphenacyl ester, m. p. and mixed m. p. 89°). A specimen of this acid prepared from 1-bromo-4:4-dimethylpentane by reaction with malonic ester boiled at 129—130°/13 mm., had n_D^{20} 1.4298 (Found: C, 68.7; H, 11.6. Calc. for $C_9H_8O_2$: C, 68.3; H, 11.5%) (Whitmore *et al.*, U.S.P., 2,032,159, give b. p. 145°/20 mm.), and gave a *p*-phenylphenacyl ester, m. p. 89° (Found: C, 78.3; H, 8.0. $C_{23}H_{28}O_2$ requires C, 78.4; H, 8.0%).

Preparation of 2:2:6:6-Tetramethyloctane.—2:2:6:6-Tetramethyloctane was obtained in poor yield by reaction of methylmagnesium iodide with 6-chloro-2:2:6-trimethyloctane.

(a) *6-Chloro-2:2:6-trimethyloctane.* The Grignard compound from 1-bromo-4:4-dimethylpentane (190.5 g.) and ethyl methyl ketone (64 g.) gave 3:7:7-trimethyloctan-3-ol (134 g.), b. p. 101—103°/21 mm., n_D^{20} 1.4339 (Found: C, 77.0; H, 14.1. $C_{11}H_{24}O$ requires C, 76.7; H, 14.0%). Saturation of the alcohol (57 g.) with dry hydrogen chloride at 0° gave a dark red upper layer, which was separated and washed successively with ice-cold sodium hydrogen carbonate solution and ice-water. It was freed from the last traces of hydrogen chloride by storage for 24 hours in a vacuum-desiccator containing sodium hydroxide. Pure 6-chloro-2:2:6-trimethyloctane (yield, 57 g.) is a colourless liquid with a pleasant odour, becoming yellow on prolonged storage; it has b. p. 48.8—49.3°/0.7 mm., n_D^{20} 1.4365 (Found: C, 69.5; H, 11.9; Cl, 18.3. $C_{11}H_{23}Cl$ requires C, 69.25; H, 12.15; Cl, 18.6%).

(b) *Reaction of 6-chloro-2:2:6-trimethyloctane with methylmagnesium iodide.* The foregoing chloride (50 g.) was added dropwise, with stirring, to a boiling filtered ethereal solution of methylmagnesium iodide (0.31 g.-mol.). A greenish-white lower layer separated. Heating and stirring were continued for 2 days. The product was isolated by adding ice and ammonium sulphate solution and distilling the dried ethereal solution through an efficient column. The following fractions were obtained: (a) b. p. 23—59°/17 mm. (0.4 g.), (b) b. p. 59—67°/17 mm. (4.4 g.), (c) b. p. 68—72.5°/17 mm. (34 g.), and (d) b. p. above 73°/17 mm. (2 g.). Fraction (c), obviously a mixture, was refluxed over sodium for 3 hours and then shaken with ten successive portions of 80% sulphuric acid till the bulk of the unsaturated hydrocarbon had been removed. Systematic fractionation through a 6' column (10—15 theoretical plates) concentrated 2:2:6:6-tetramethyloctane into the fraction, b. p. 182.2—183.3°. It still contained some olefin; this was removed by percolation through a column packed with silica gel till the refractive index was not further altered (n_D^{20} 1.4203) (Found: C, 84.5; H, 15.05. $C_{12}H_{26}$ requires C, 84.6; H, 15.4%).

The following alcohols were prepared by reaction of the appropriate alkylmagnesium bromide with the appropriate ketone:

3:7:7-Trimethylnonan-3-ol, b. p. 62—73°/0.6 mm., n_D^{15} 1.4431 (yield 77%) (Found: C, 77.0; H, 13.9. $C_{12}H_{26}O$ requires C, 77.4; H, 14.1%).

2:2:6-Trimethylundecan-6-ol, b. p. 126—128°/11 mm., n_D^{20} 1.4418 (yield 67%) (Found: C, 78.6; H, 14.3. $C_{14}H_{30}O$ requires C, 78.4; H, 14.1%).

3:10:10-Trimethylundecan-3-ol, b. p. 97°/0.8 mm., n_D^{20} 1.4437 (yield 68%) (Found: C, 78.2; H, 13.8. $C_{14}H_{30}O$ requires C, 78.4; H, 14.1%).

2:2:6-Trimethylpentadecan-6-ol, b. p. 136—137°/0.5 mm., n_D^{20} 1.4480 (yield 66%) (Found: C, 80.4; H, 14.2. $C_{18}H_{38}O$ requires C, 80.0; H, 14.2%).

Preparation of Paraffins with Two Quaternary Carbon Atoms by the Gardner-Bergstrom Reaction.—(a) 2:2:9:9-Tetramethyldecane. The filtered Grignard compound from 1-bromo-4:4-dimethylpentane (0.125 g.-mol.) was treated in ice-cold ether with dry silver bromide with constant stirring. The reaction was completed by 1 hour's heating under reflux. 2:2:9:9-Tetramethyldecane was isolated by distillation of the filtered reaction mixture, drying, and then shaking it successively with several small volumes of sulphuric acid. The product distilled over sodium at 93°/10 mm. and had n_D^{20} 1.4250 (Found: C, 85.15; H, 15.2. $C_{14}H_{30}$ requires C, 84.75; H, 15.25%).

(b) 3:3:10:10-Tetramethyldecane. This hydrocarbon, b. p. 127°/10 mm., n_D^{20} 1.4388 (Found: C, 85.0; H, 15.3. $C_{16}H_{34}$ requires C, 84.9; H, 15.1%), was similarly prepared.

(c) 2:2:15:15-Tetramethylhexadecane. This compound had b. p. 134°/0.4 mm., n_D^{20} 1.4401 (Found: C, 85.5; H, 14.85. $C_{20}H_{42}$ requires C, 85.0; H, 15.0%).

Preparation of Paraffins with Two or Three Quaternary Carbon Atoms from the Corresponding Alcohols.—(a) 2:2:6:10:10-Pentamethylundecane. The Grignard compound from 1-bromo-4:4-dimethylpentane (0.8 g.-mol.) reacted with an ethereal solution of ethyl acetate (0.32 g.-mol.), to give 2:2:6:10:10-pentamethylundecan-6-ol, b. p. 122—124°/4 mm., m. p. 64.5 [from light petroleum (b. p. 40—60°)] (54 g.) (Found: C, 79.1; H, 14.1. $C_{16}H_{34}O$ requires C, 79.3; H, 14.1%).

Dehydration of the alcohol (50.5 g.) was effected by heating it at 180° for 3 hours with an equimolecular proportion of phthalic anhydride in a flask fitted with a reflux condenser and an adjustable take-off to remove the water as it was formed. The resulting olefin was refluxed over sodium before fractionation and then had b. p. 122—127°/19 mm., n_D^{20} 1.4408—1.4410 (yield, 35 g.) (Found: C, 85.8; H, 14.3. $C_{14}H_{28}$ requires C, 85.6; H, 14.4%). Ozonolysis of a portion (15 g.) gave formaldehyde (dimeric derivative, m. p. and mixed m. p. 190°), 6:6-dimethylheptan-2-one (8.5 g.), n_D^{20} 1.4188—1.4232 (semicarbazone, m. p. and mixed m. p. 180—181°), 2:2:10:10-tetramethylundecane-6-one (0.3 g.), n_D^{20} 1.4320 (semicarbazone, m. p. and mixed m. p. 131°), and neopentylacetic acid, b. p. 121°/29 mm., n_D^{20} 1.4201 (6.3 g.) [amide, m. p. and mixed m. p. 139—140° (Whitmore and Homeyer, *J. Amer. Chem. Soc.*, 1933, 55, 4555); *S*-benzylthiuronium salt, m. p. and mixed m. p. 154.5°]. The olefin thus consists essentially of 2:2:6:10:10-pentamethylundec-5-ene with a small proportion of 6:6-dimethyl-2-(4:4-dimethylpentyl)hept-1-ene.

Hydrogenation of the olefin (Raney nickel; ethyl alcohol; 100°/30 atms.) gave 2:2:6:10:10-pentamethylundecane, b. p. 80.5°/0.5 mm., n_D^{20} 1.4299 (76%) (Found: C, 85.15; H, 15.05. $C_{16}H_{34}$ requires C, 84.9; H, 15.1%).

(b) 3 : 3 : 7 : 11 : 11-Pentamethyltridecane. The Grignard compound from 1-bromo-4 : 4-dimethylhexane (0.4 g.-mol.), and ethyl acetate (0.17 g.-mol.) gave some low-boiling material (7.5 g.) and 3 : 3 : 7 : 11 : 11-pentamethyltridecan-7-ol, m. p. 39.5°, b. p. 126—126.5°/1.8 mm. (32 g.) (Found : C, 79.8; H, 14.4. $C_{18}H_{38}O$ requires C, 79.9; H, 14.2%).

This was dehydrated with phthalic anhydride at 180° to give an olefin, b. p. 146—148°/10 mm., n_D^{20} 1.4515—1.4519 (Found : C, 85.7; H, 14.4. $C_{18}H_{36}$ requires C, 85.6; H, 14.4%), consisting largely of 3 : 3 : 7 : 11 : 11-pentamethyltridec-6-ene with a little 6 : 6-dimethyl-2-(4 : 4-dimethylhexyl)oct-1-ene. It gave, on ozonolysis, formaldehyde (dimedone derivative, m. p. and mixed m. p. 189°), 6 : 6-dimethyloctan-2-one (semicarbazone, m. p. and mixed m. p. 143.5—144.5°; cf. below), and 3 : 3-dimethylpentane-1-carboxylic acid (S-benzylthiuronium salt, m. p. and mixed m. p. 152°); a small fraction corresponding to 3 : 3 : 11 : 11-tetramethyltridecan-7-one was obtained but it could not be purified sufficiently for exact characterisation.

Hydrogenation of the olefin (Raney nickel; ethyl alcohol; 100°/40 atms.; 4 hours) gave 3 : 3 : 7 : 11 : 11-pentamethyltridecane (65%), b. p. 101°/0.35 mm., n_D^{20} 1.4419, d_{15}^{20} 0.7911 (Found : C, 84.6; H, 14.95. $C_{18}H_{38}$ requires C, 84.95; H, 15.05%).

(c) 2 : 2 : 10 : 10-Tetramethyl-6-(4 : 4-dimethylpentyl)undecane. The Grignard compound from 1-bromo-4 : 4-dimethylpentane (0.15 g.-mol.) and ethyl 4 : 4-dimethylpentane-1-carboxylate (0.06 g.-mol.) gave 2 : 2 : 10 : 10-tetramethyl-6-(4 : 4-dimethylpentyl)undecan-6-ol (57%), m. p. 48°, b. p. 140.5°/0.8 mm. (Found : C, 81.25; H, 14.45. $C_{22}H_{46}O$ requires C, 80.9; H, 14.2%). Heating the alcohol with iodine caused dehydration to 2 : 2 : 10 : 10-tetramethyl-6-(4 : 4-dimethylpentyl)undec-5-ene (77%), b. p. 112—113°/0.6 mm., n_D^{20} 1.4464 (Found : C, 85.8; H, 14.45. $C_{22}H_{44}$ requires C, 85.6; H, 14.4%). Ozonolysis in chloroform gave 2 : 2 : 10 : 10-tetramethylundecan-6-one (semicarbazone, m. p. and mixed m. p. 131.5—132.5°) and neopentylacetic acid (amide, m. p. and mixed m. p. 138—139°). Hydrogenation of the olefin (Raney nickel; ethyl alcohol; 104—140°/75 atms.) gave 2 : 2 : 10 : 10-tetramethyl-6-(4 : 4-dimethylpentyl)undecane (80%), b. p. 121°/0.4 mm., n_D^{20} 1.4414, d_{20}^{20} 0.7882 (Found : C, 85.45; H, 14.6. $C_{22}H_{46}$ requires C, 85.1; H, 14.9%).

For the identification of the products of the ozonolysis of the olefins described above, the following reference compounds were prepared.

1-Cyano-4 : 4-dimethylpentane, b. p. 88—89°/24 mm., n_D^{20} 1.4194 (Found : C, 76.6; H, 11.8; N, 11.2. $C_8H_{15}N$ requires C, 76.7; H, 12.1; N, 11.2%), was obtained in 74% yield by the reaction of 1-bromo-4 : 4-dimethylpentane with aqueous-alcoholic potassium cyanide. With methylmagnesium iodide it yielded 6 : 6-dimethylheptan-2-one, b. p. 78—79°/22 mm., n_D^{19} 1.4225 (Found : C, 75.5; H, 12.3. $C_9H_{18}O$ requires C, 76.1; H, 12.7%) [2 : 4-dinitrophenylhydrazone, m. p. 107—108° (Found : C, 56.0; H, 6.6. $C_{15}H_{22}O_4N_4$ requires C, 55.9; H, 6.9%)]. Hydrolysis of the nitrile gave 4 : 4-dimethylpentane-1-carboxylic acid (84%), b. p. 126—129°/21 mm., m. p. 39° (Found : C, 67.1; H, 10.8. Calc. for $C_8H_{16}O_2$: C, 66.7; H, 11.1%) (Whitmore *et al.*, U.S.P., 2,032,159, give b. p. 130°/20 mm., m. p. 38°) [amide, m. p. 97—98° (Found : N, 9.6. $C_8H_{17}ON$ requires N, 9.8%)]. The chloride, b. p. 79—82°/22 mm., obtained from the acid in 79% yield by the action of thionyl chloride, reacted in benzene solution with di-(4 : 4-dimethylpentyl)cadmium to give 2 : 2 : 10 : 10-tetramethylundecan-6-one (51%), b. p. 132°/10 mm., n_D^{20} 1.4353 (Found : C, 79.4; H, 13.2. $C_{18}H_{36}O$ requires, C, 79.6; H, 13.4%) [semicarbazone, m. p. 131.5—132.5° (Found : C, 680; H, 11.6; N, 14.8. $C_{18}H_{36}ON_2$ requires C, 67.8; H, 11.7; N, 14.8%)].

Di-(4 : 4-dimethylhexyl)cadmium and acetyl chloride in benzene gave 6 : 6-dimethyloctan-2-one, which was purified through its semicarbazone, m. p. 145—146° (Found : C, 62.4; H, 10.9. $C_{11}H_{22}ON_2$ requires C, 61.9; H, 10.9%). The pure ketone had b. p. 96°/33 mm., n_D^{20} 1.4289 (Found : C, 77.1; H, 13.0. $C_{10}H_{20}O$ requires C, 76.9; H, 12.9%).

3 : 3 : 11 : 11-Tetramethyltridecan-7-one, b. p. 114—115°/0.4 mm., n_D^{19} 1.4488, was prepared in 54% yield by reaction of di-(4 : 4-dimethylhexyl)cadmium and 4 : 4-dimethylhexane-1-carboxyl chloride. It was characterised by its semicarbazone, m. p. 108° (Found : C, 6902; H, 11.8; N, 13.3. $C_{18}H_{37}ON_2$ requires C, 69.4; H, 12.0; N, 13.5%). 4 : 4-Dimethylhexane-1-carboxylic acid, required for this preparation, was obtained by the alkaline hydrolysis of 1-cyano-4 : 4-dimethylhexane. The free acid had b. p. 128.5—130°/9 mm., n_D^{20} 1.4362 (Found : C, 68.4; H, 11.3. $C_8H_{18}O_2$ requires C, 68.3; H, 11.5%), and gave a S-benzylthiuronium salt, m. p. 146°, and an acid chloride, b. p. 82—84°/10.5 mm., n_D^{20} 1.4423. 1-Cyano-4 : 4-dimethylhexane was prepared in 76% yield by the reaction of 1-bromo-4 : 4-dimethylhexane with potassium cyanide in aqueous-alcoholic solution; it had b. p. 88—90°/10 mm., n_D^{20} 1.4298 (Found : C, 77.7; H, 12.35; N, 10.4. $C_9H_{17}N$ requires C, 77.6; H, 12.3; N, 10.1%).

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