458. *The Synthesis and Reactions of Branched-chain Hydrocarbons. Part I. Hydrocarbons with the 3 : 5 : 5-Trimethylhexyl Group.*

By E. M. Gutman and W. J. Hickinbottom.

The preparation of 2 : 2 : 4 : 7 : 10 : 12 : 12-heptamethyltridecan-7-ol and of 2 : 2 : 4 : 10 : 12 : 12-hexamethyl-7-(3 : 5 : 5-trimethylhexyl)tridecan-7-ol is described. By successive dehydration and hydrogenation 2 : 2 : 4 : 7 : 10 : 12 : 12-heptamethyltridecane and 2 : 2 : 4 : 10 : 12 : 12-hexamethyl-7-(3 : 5 : 5-trimethylhexyl)tridecane are obtained. Ozonolysis of the olefins is described. 2 : 2 : 4 : 9 : 11 : 11-Hexamethyldodecane is prepared by the action of silver bromide on the Grignard compound from 1-chloro-3 : 5 : 5-trimethylhexane.

This paper is the first of a series which has for its object the study of the reactions and properties of paraffins with a regular pattern of quaternary carbon atoms. A necessary preliminary is the development and exploitation of methods for the unambiguous synthesis of hydrocarbons of suitable structure.

The method which so far has been most useful for the direct synthesis of hydrocarbons with a quaternary carbon atom consists in the reaction of an alkyl halide with a suitable metal alkyl. Zinc alkyls have been used successfully for this purpose (Friedel and Ladenburg, *Annalen*, 1867, **142**, 310; Goriainow, *ibid.*, 1873, **165**, 107; Markownikoff, *Ber.*, 1899, **32**, 1445; 1900, **33**, 1905; Noller, *J. Amer. Chem. Soc.*, 1929, **51**, 594). Their value for the present work is seriously impaired by partial isomerisation which occurs during the reaction if highly branched compounds are used (Buck, Elsner, *et al.*, *J. Inst. Petr.*, 1948, **34**, 339). The risk of isomerisation is reduced if alkylmagnesium halides are used instead of zinc alkyls, but their use is attended by the inconvenience of low yields and of the presence of a considerable proportion of other products.

One suitable line of approach is to use in usual synthetic reactions alkylmagnesium halides having quaternary carbon atoms. It is one of the primary objects of this work to explore the possibilities and limitations of such compounds.

1-Chloro-3 : 5 : 5-trimethylhexane seemed a suitable compound for this purpose, in that it can be prepared in good yield from the readily accessible 3 : 5 : 5-trimethylhexan-1-ol. It appears from qualitative observations that the chloride is not very reactive; for its hydrolysis, prolonged boiling with aqueous alkali is necessary; potassium cyanide yields the corresponding nitrile slowly and only after long boiling. It reacts sluggishly in ether with magnesium to form the corresponding Grignard compound. Under suitable conditions a yield of about 80% of the alkylmagnesium chloride is obtained and the solution so formed reacts smoothly and normally with esters of carboxylic acids to give tertiary alcohols. The present paper describes the preparation of 2 : 2 : 4 : 7 : 10 : 12 : 12-heptamethyltridecan-7-ol (I) and 2 : 2 : 4 : 10 : 12 : 12-hexamethyl-7-(3 : 5 : 5-trimethylhexyl)tridecan-7-ol (IV). These alcohols are dehydrated to the olefins (II) and (III) from the first and (V) from the second without change of structure by heating them with a small amount of iodine.

$(CMe_3{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2)_2CMe{\cdot}OH$
(I.)

$CMe_3{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CMe_3$
(II.)

$(CMe_3{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2)_2C{:}CH_2$
(III.)

$(CMe_3{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2)_3C{\cdot}OH$
(IV.)

$(CMe_3{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2)_2C{:}CH{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CMe_3$
(V.)

$(CMe_3{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2)_2$
(VI.)

The structure of these olefins was established by ozonolysis and comparison of the products so obtained with synthetic specimens.

The Grignard compound from 1-chloro-3 : 5 : 5-trimethylhexane reacts with dry silver bromide to give 2 : 2 : 4 : 9 : 11 : 11-hexamethyldodecane (VI); in this reaction a notable proportion of an olefin was also formed.

EXPERIMENTAL.

(Analyses by Drs. Weiler and Strauss.)

Preparation of 1-*Chloro*-3 : 5 : 5-*trimethylhexane*.—3 : 5 : 5-Trimethylhexan-1-ol, a gift from Imperial Chemicals Industries Limited, Billingham, had the following constants: b. p. 85°/11 mm., n_D^{20} 1·4330; it was characterised by its 3 : 5-dinitrobenzoate, m. p. 63°, and its 3-nitrophthalic hydrogen ester, m. p. 150°.

The alcohol (144 g.), diluted with dry pyridine (79 g.), was cooled in ice and mechanically stirred while redistilled thionyl chloride (125 g.) was added gradually. An exothermic reaction developed and a bulky solid separated. When the addition had been completed, stirring was continued for a further 20 minutes. The reaction mixture was then gradually heated to 110° and kept at this temperature till the evolution of sulphur dioxide had ceased (2—4 hours). The product was isolated by pouring the mixture into water and washing the organic layer successively with water, dilute sulphuric acid, aqueous sodium carbonate, and water. The dried liquid on fractionation through an efficient column gave pure 1-*chloro*-3 : 5 : 5-*trimethylhexane*, b. p. 70°/17 mm., n_D^{20} 1·4332 (yield 147 g., 91%) (Found: C, 66·4; H, 11·5; Cl, 21·9, 22·0. $C_9H_{19}Cl$ requires C, 66·4; H, 11·8; Cl, 21·8%). Bruner (*Ind. Eng. Chem.*, 1949, **41**, 2861) gives b. p. 179—180°/760 mm., n_D^{25} 1·4304, for this chloride prepared by the action of hydrogen chloride on the alcohol at 135°, but does not give an analysis.

The chloride is hydrolysed very slowly by aqueous alkali; it reacts only sluggishly in ether with magnesium. From 0·2 g.-mol. of chloride, the corresponding Grignard compound was prepared in 78% yield, after the reaction had been started by the addition of 4 drops of methyl iodide. Oxidation of the Grignard compound in ether by molecular oxygen gave 3 : 5 : 5-trimethylhexan-1-ol, b. p. 80—85°/12 mm., $n_D^{20.5}$ 1·4329—1·4332 (67% calculated on the chloride used); its 3 : 5-dinitrobenzoate had m. p. and mixed m. p. 63°. 1-*Bromo*-3 : 5 : 5-*trimethylhexane*, b. p. 75°/12 mm., n_D^{20} 1·4527, was isolated in 70% yield by refluxing the alcohol (19·8 g.) with hydrobromic acid (48%, 60 g.) and concentrated sulphuric acid (15·5 g.) for 6 hours (Found: C, 52·8; H, 9·2; Br, 38·2. $C_9H_{19}Br$ requires C, 52·2; H, 9·2; Br, 38·6%) (Bruner, *loc. cit.*, gives b. p. 70—71°/11 mm., n_D^{25} 1·4510, for the bromide prepared by the action of hydrogen bromide at 150°, but gives no analysis).

Preparation of 2 : 2 : 4 : 7 : 10 : 12 : 12-*Heptamethyltridecane*.—The Grignard reagent [from 1-chloro-3 : 5 : 5-trimethylhexane (65 g., 0·4 mol.), magnesium (9·8 g.), and ether (150 ml.)] was added to ethyl acetate (14·4 g., 0·16 mol.), and the reaction completed by heating the mixture under reflux. The product was decomposed by ice and ammonium chloride, and the washed ethereal solution fractionally distilled. 2 : 2 : 4 : 7 : 10 : 12 : 12-*heptamethyltridecan*-7-*ol* (I) was collected at 124—126°/0·9 mm.; the yield was 38 g. (78%). The pure alcohol is a colourless viscous oil, b. p. 120°/0·5 mm., n_D^{20} 1·4512 (Found: C, 80·5; H, 13·7. $C_{20}H_{42}O$ requires C, 80·5; H, 14·1%).

Dehydration was effected by heating the alcohol (28 g.) with a few crystals of iodine in a flask fitted with a reflux condenser and a partial take-off head, till no more water was collected (1·1 ml.) ($\frac{1}{2}$ hour). The residue, after being washed with water and thiosulphate solution, was dried and refluxed over sodium for 3 hours. It distilled at 101—103°/0·55 mm., n_D^{20} 1·4389—1·4398, and consisted largely of 2 : 2 : 4 : 7 : 10 : 12 : 12-*heptamethyltridec*-6-*ene* (II) with a small proportion of 5 : 7 : 7-trimethyl-2-(3 : 5 : 5-trimethylhexyl)oct-1-ene (III) (Found: C, 85·8; H, 14·1. $C_{20}H_{40}$ requires C, 85·6; H, 14·4%).

Ozonolysis of the olefin (22 g.) in chloroform gave formaldehyde (dimedone derivative, m. p. and mixed m. p. 189°) and 5 : 7 : 7-trimethyloctan-2-one (b. p. 92—101°/32 mm., 8·5 g.; n_D^{20} 1·4284—1·4292), which formed a 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 79°. Systematic fractionation of the higher-boiling fractions of the neutral product of ozonolysis gave a further amount of the above ketone (1·8 g.) and a small fraction (0·6 g.), b. p. 120—134°/1·3 mm., having characteristics similar to those of 2 : 2 : 4 : 10 : 12 : 12-hexamethyltridecan-7-one although no crystalline derivatives could be prepared from it. The acidic product of the ozonolysis boiled at 126—129°/15 mm. (4·6 g.), $n_D^{20·1}$ 1·4297, and was identified as 2 : 4 : 4-trimethylpentane-1-carboxylic acid by its physical constants (the pure acid given by Imperial Chemical Industries Limited, Billingham, had b. p. 125°/12 mm., $n_D^{20·1}$ 1·4295) and its S-*benzylthiuronium* salt, m. p. and mixed m. p. 154° (Found : C, 63·2; H, 8·6; N, 8·4. $C_{17}H_{28}O_2N_2S$ requires C, 62·9; H, 8·6; N, 8·6%).

Hydrogenation of the olefin (20 g.) in ethyl alcohol (Raney nickel at 150°/39 atm.) gave 2 : 2 : 4 : 7 : 10 : 12 : 12-*heptamethyltridecane*. It was purified from traces of olefin by percolating the distilled hydrocarbon through a column of silica gel followed by a further fractionation and had b. p. 112°/0·5 mm. (16 g., 79%), n_D^{20} 1·4437, d_{19}^{19} 0·7901 (Found : C, 85·0; H, 14·65. $C_{20}H_{42}$ requires C, 85·0; H, 15·0%).

5 : 7 : 7-*Trimethyloctan*-2-*one*.—For purposes of comparison this ketone was prepared, but not in very good yield, by two methods.

(i) 1-Cyano-3 : 5 : 5-trimethylhexane (5·3 g.) in ether (15 ml.) was added slowly to a solution prepared from methyl iodide (5·85 g.), magnesium (1 g.), and ether (15 ml.). A gentle reaction occurred and it was completed by heating the solution under reflux for 1 hour. Decomposition of the product with aqueous acid and fractionation gave 5 : 7 : 7-trimethyloctan-2-one (1·6 g.), b. p. 103°/28 mm., n_D^{20} 1·4309, and unidentified higher-boiling material (2·4 g.).

(ii) The filtered Grignard reagent from 1-chloro-3 : 5 : 5-trimethylhexane (19·5 g.) and magnesium (2·95 g.) in ether was stirred and refluxed with finely powdered cadmium chloride (12·8 g.) for 3 hours. The ether was removed next morning and replaced by benzene (70 ml.). A solution of acetyl chloride (7·6 g.) in dry benzene (20 ml.) was added slowly, and the mixture stirred and heated. After 3 hours the orange-coloured, viscous reaction product was decomposed by aqueous sulphuric acid, and the benzene layer fractionally distilled to give crude 5 : 7 : 7-trimethyloctan-2-one (6·1 g.), b. p. 94—100°/22 mm., n_D^{20} 1·4346—1·4359.

The pure *ketone*, b. p. 103°/28 mm., n_D^{20} 1·4309 (Found : C, 78·0; H, 13·0. $C_{11}H_{22}O$ requires C, 77·6; H, 13·0%), was purified through its semicarbazone, m. p. 147·5—148·5°, and 2 : 4-*dinitrophenylhydrazone*, m. p. 80° (Found : C, 58·6; H, 7·2; N, 15·5. $C_{17}H_{26}O_4N_4$ requires C, 58·3; H, 7·4; N, 16·0%).

3 : 3 : 5-*Trimethylhexane*-1-*carboxylic Acid*.—A solution of potassium cyanide (78 g.) in water (75 ml.) and alcohol (170 ml.) was refluxed with 1-chloro-3 : 5 : 5-trimethylhexane (97·5 g.) for 72 hours. Fractionation of the water-insoluble product gave the required *nitrile* (59·5 g.), b. p. 97—98°/11 mm., $n_D^{20·7}$ 1·4294 (Found : C, 78·1; H, 12·55; N, 9·1. $C_{10}H_{19}N$ requires C, 78·4; H, 12·5; N, 9·1%). Hydrolysis of the nitrile (20 g.) with hot aqueous-alcoholic sodium hydroxide for 24 hours gave, after acidification, 3 : 5 : 5-*trimethylhexane*-1-*carboxylic acid* (19·8 g.), b. p. 132—133°/8 mm., $n_D^{21·2}$ 1·4346 (Found : C, 69·6; H, 11·6. $C_{10}H_{20}O_2$ requires C, 69·7; H, 11·7%). Its S-*benzylthiuronium* salt had m. p. 155° (Found : N, 8·2; S, 9·0. $C_{18}H_{30}O_2N_2S$ requires N, 8·2; S, 9·4%); the chloride had b. p. 104°/22 mm., n_D^{20} 1·4411; the *amide* m. p. 107° (Found : C, 70·1; H, 12·3; N, 8·3. $C_{10}H_{21}ON$ requires C, 70·0; H, 12·3; N, 8·2%); and the *ethyl* ester b. p. 96·5°/9 mm., $n_D^{21·2}$ 1·4254 (Found : C, 72·4; H, 11·75. $C_{12}H_{24}O_2$ requires C, 72·0; H, 12·0%).

2 : 2 : 4 : 10 : 12 : 12-*Hexamethyl*-7-(3 : 5 : 5-*trimethylhexyl*)*tridecane*.—The foregoing ethyl ester (40 g.) in ether (60 ml.) was added dropwise to a Grignard reagent prepared from 1-chloro-3 : 5 : 5-trimethylhexane (80·5 g.), magnesium (12·15 g.), and dry ether (150 ml.). The reaction was completed by warming the mixture under reflux for 1 hour, and the product was then decomposed with ice and ammonium chloride acidified with hydrochloric acid. Distillation gave some unchanged chloride, some 3 : 5 : 5-trimethylhexan-1-ol, and a main fraction consisting of 2 : 2 : 4 : 10 : 12 : 12-*hexamethyl*-7-(3 : 5 : 5-*trimethylhexyl*)*tridecan*-7-*ol* (IV), b. p. 176—178°/0·8 mm., n_D^{20} 1·4558—1·4559 (60 g.) (Found : C, 82·0; H, 13·8. $C_{28}H_{58}O$ requres C, 81·9; H, 14·2%), a viscous oil.

Dehydration was effected by heating the alcohol (40 g.) with a few crystals of iodine at 200° for 3 hours, although it seemed from the amount of water evolved that the reaction was substantially complete within 15 minutes. The olefin, 2 : 2 : 4 : 10 : 12 : 12-*hexamethyl*-7-(3 : 5 : 5-*trimethylhexyl*)-*tridec*-7-*ene*, after being washed with thiosulphate solution and refluxed over sodium, distilled at 161—162°/0·8 mm. as a colourless viscous liquid (31 g.), $n_D^{20·4}$ 1·4548—1·4549 (Found : C, 85·6; H, 14·2. $C_{28}H_{56}$ requires C, 85·6; H, 14·4%).

Ozonolysis of the olefin (8·6 g.) in chloroform gave 2 : 2 : 4 : 10 : 12 : 12-hexamethyltridecan-7-one (1·9 g.), b. p. 124—127°/0·8 mm., characterised by its semicarbazone, m. p. and mixed m. p. 69°, and 2 : 4 : 4-trimethylpentane-1-carboxylic acid (2·8 g.), b. p. 128—131°/16 mm., $n_D^{20·3}$ 1·4292, which gave an S-benzylthiuronium salt, m. p. and mixed m. p. 154°.

Hydrogenation of the olefin (30·5 g.) in ethyl alcohol (150 ml.) (Raney nickel at 180°/27 atm.) gave 2 : 2 : 4 : 10 : 12 : 12-*hexamethyl*-7-(3 : 5 : 5-*trimethylhexyl*)*tridecane*. This was freed from traces of unchanged olefin by passing its solution in heptane (15 ml.) through a column filled with silica gel and subsequent fractionation; the pure hydrocarbon (24·1 g., 78%) had b. p. 166°/0·5 mm., n_D^{20} 1·4558, d_{20}^{20} 0·8152 (Found : C, 85·3; H, 14·8. $C_{28}H_{58}$ requires C, 85·2; H, 14·8%).

2 : 2 : 4 : 10 : 12 : 12-*Hexamethyltridecan*-7-*one* was prepared in 68% yield by reaction of the chloride from 3 : 5 : 5-trimethylhexanecarboxylic acid (20·5 g.) with di-(3 : 5 : 5-trimethylhexyl)cadmium [from

the Grignard reagent from 1-chloro-3 : 5 : 5-trimethylhexane (31 g.) in benzene]. It had b. p. 124°/1·1 mm., n_D^{20} 1·4460 (Found : C, 81·2; H, 13·4. $C_{19}H_{38}O$ requires C, 80·8; H, 13·5%); *semicarbazone*, m. p. 69° (Found : N, 12·3. $C_{20}H_{41}ON_3$ requires N, 12·4%); its 2 : 4-dinitrophenylhydrazone had m. p. 39°.

2 : 2 : 4 : 9 : 11 : 11-*Hexamethyldodecane.*—To the filtered and cooled Grignard reagent from 1-chloro-3 : 5 : 5-trimethylhexane (32·5 g.) was added dry silver bromide (37·6 g.) (Gardner and Bergstrom, *J. Amer. Chem. Soc.*, 1929, **51**, 3375). The solution became black and silver was precipitated. Efficient stirring was maintained throughout the addition and for 1 hour after all the silver bromide had been added. The reaction was completed by heating under reflux for 1 hour. Distillation after removal of inorganic material gave low-boiling material (7·5 g.), b. p. 39—70°/11 mm., and 2 : 2 : 4 : 9 : 11 : 11-*hexamethyldodecane*, b. p. 136°/8 mm. (8·2 g.). Traces of olefin were removed by shaking it with small amounts of concentrated sulphuric acid, and the purification completed by refluxing over sodium; b. p. 138·5°/10 mm., n_D^{20} 1·4370 (Found : C, 84·7; H, 15·05. $C_{18}H_{38}$ requires C, 84·95; H, 15·05%).

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