382. *The Synthesis and Reactions of Branched-chain Hydrocarbons. Part XI.** 2 : 2 : 4 : 6 : 6-*Pentamethylhept*-3-*ene, One of the Constituents of Triïsobutylene.*

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Pyrolysis of the stearates of 2 : 2 : 4 : 6 : 6-pentamethylhepten-3-ol, 2 : 2 : 4-trimethylhexan-3-ol and 4-ethyl-2 : 2-dimethylhexan-3-ol gives the corresponding olefins without rearrangement or without migration of the double bond. The addition of some pyridine to the ester before pyrolysis was found to be necessary.

It has been established,[1] from examination of the products of ozonolysis and oxidation, that technical tri*iso*butylene is a mixture of four isomeric dodecenes (I—IV). The main constituents are (I) and (II), present in about equal amounts; (III) and (IV) together comprise about 10% of the technical product, although some wide variation in the relative proportions occurs. No satisfactory separation of any one constituent has yet been achieved by distillation. It has however been possible to isolate *as*-di*neo*pentylethylene (I) in a pure state by taking advantage of the fact that it is more resistant to oxidation than its isomers.[2] It is also reported that components (III) and (IV) can be separated from technical tri*iso*butylene by their more ready combination with hydrogen chloride.[3]

$$(\mathrm{Me_3C{\cdot}CH_2})_2\mathrm{C{:}CH_2} \quad (\mathrm{I}) \qquad \mathrm{Me_3C{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}CMe_3} \quad (\mathrm{II}) \qquad \mathrm{Me_3C{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}CMe{:}CH_2} \quad (\mathrm{III})$$

$$\mathrm{Me_3C{\cdot}CH_2{\cdot}CMe_2{\cdot}CH{:}CMe_2} \quad (\mathrm{IV}) \qquad \mathrm{Me_3C{\cdot}CH(OH){\cdot}CHRR'} \quad (\mathrm{V})$$

For another investigation it was necessary to have a considerable quantity of 2 : 2 : 4 : 6 : 6-pentamethylhept-3-ene (II) in a pure state. A satisfactory method appeared to consist in the dehydration of 2 : 2 : 4 : 6 : 6-pentamethylheptan-3-ol (V; $\mathrm{R} = \mathrm{Me}$, $\mathrm{R}' = \mathrm{CH_2{\cdot}CMe_3}$) by thermal decomposition of its carboxylic esters or its methylxanthate. It is known already that these methods can be applied successfully to the preparation of *tert.*-butylethylene from 3 : 3-dimethylbutan-2-ol without rearrangement of the sensitive *neo*pentyl group.[4] In the projected method of preparation of (II), bond migration is also possible. Accordingly preliminary experiments were carried out on simpler alcohols having the same structural features (V; $\mathrm{R} = \mathrm{Me}$, $\mathrm{R}' = \mathrm{Et}$; or $\mathrm{R} = \mathrm{R}'$

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* Part X, *J.*, 1956, 911.

[1] McCubbin, *J. Amer. Chem. Soc.*, 1931, **53**, 356; Whitmore *et al.*, *ibid.*, 1941, **63**, 2035, 2200.

[2] Bartlett, Frazer, and Woodward, *ibid.*, p. 495; Hickinbottom and Wood, *J.*, 1951, 1601.

[3] U.S.P. 2,485,265.

[4] Dolliver, Gresham, Kistiakowsky, and Vaughan, *J. Amer. Chem. Soc.*, 1937, **59**, 832; Stevens and Richmond, *ibid.*, 1941, **63**, 3135.

= Et). It was found that pyrolysis of the stearates of these alcohols gave the required olefins if some pyridine was added. If this were omitted, the product boiled over a range of several degrees and no steady refractive index could be obtained. The olefins (II) and that from (V; R = Me, R′ = Et) boiled over a range of 0·5—1·0° and the refractive index drifted about 0·0007—0·0010 unit. This variation can be reasonably attributed to the presence of *cis*- and *trans*-isomers, since only the expected fission products were obtained from ozonolysis; further support for this view is provided by the observation that from (V; R = R′ = Et), where there is no possibility of *cis-trans*-isomerism, the olefin was of almost constant b. p. and n_D^{20}.

EXPERIMENTAL

2 : 2 : 4 : 6 : 6-*Pentamethylhept*-3-*ene*.—2 : 2 : 4 : 6 : 6-Pentamethylheptan-3-ol was prepared essentially by the method of Whitmore *et al.*[5] from 2 : 4 : 4-trimethylpentanoyl chloride with an excess of *tert.*-butylmagnesium chloride; 379 g. of acid chloride gave 2 : 2 : 4 : 6 : 6-pentamethylheptan-3-ol (488 g.), b. p. 100—102°/21 mm., n_D^{20} 1·4420, and 2 : 2 : 4-trimethylpentan-1-ol (121 g.), b. p. 79—80°/23 mm., n_D^{20} 1·4285—1·4270.

2 : 2 : 4 : 6 : 6-Pentamethylheptan-3-ol (84 g.) was added, in one portion, to stearoyl chloride (from 142 g. of stearic acid and 60 g. of thionyl chloride) and heated in a steam-bath for 12 hr. Ethyl alcohol (5 g.) was then added and heating continued for 1 hr. and then under reduced pressure to remove volatile matter. The ester formed was diluted with ether (250 c.c.) and washed with water till neutral to litmus. A final washing with saturated sodium chloride solution helped to clear the heavy emulsion which had formed. The dried ether solution ($CaCl_2$) was concentrated under reduced pressure and then heated in a metal-bath at 360° for 1 hr. after addition of 2 c.c. of pyridine. The distillate was shaken with 20% aqueous sodium hydroxide, then treated with calcium chloride solution to precipitate all the stearic acid which had distilled over with the olefin. The crude olefin was isolated by steam-distillation. The crude hydrocarbon (37 g.) had b. p. 178—181°, n_D^{20} 1·4370—1·4380. Repetition on a 2-mole scale gave 172 g. of crude olefin, b. p. 178—181°. Further distillation gave pure 2 : 2 : 4 : 6 : 6-*pentamethylhept*-3-*ene*, b. p. 180·5°, n_D^{20} 1·4370 (Found: C, 85·7; H, 14·4. $C_{12}H_{24}$ requires C, 85·6; H, 14·4%).

Ozonolysis of the olefin in chloroform and treatment of the ozonide with water and 30% hydrogen peroxide gave trimethylacetic acid (anilide, m. p. and mixed m. p. 134°) and 4 : 4-dimethylpentan-2-one (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 99—100°), together with a small amount of trimethylacetaldehyde (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 210°).

The components of all mixtures of carbonyl compounds obtained in this work, from ozonolysis or by oxidative fission of glycols, were separated and identified as their 2 : 4-dinitrophenylhydrazones by chromatography on silica or alumina, with benzene–light petroleum for elution.

The olefin with perbenzoic acid in chloroform gave 3 : 4-*epoxy*-2 : 2 : 4 : 6 : 6-*pentamethylheptane*, b. p. 71°/12 mm., n_D^{20} 1·4308 (Found: C, 78·1; H, 13·0. $C_{12}H_{24}O$ requires C, 78·2; H, 13·1%). It is hydrated when shaken with cold dilute sulphuric acid, to the glycol and other products. The epoxide (2 g.) and 0·5% sulphuric acid (25 c.c.) after 20 hr. gave a viscid oil (0·3 g.). Its identity as 2 : 2 : 4 : 6 : 6-pentamethylheptane-3 : 4-diol was confirmed by oxidative fission to trimethylacetaldehyde and methyl *neo*pentyl ketone; no other carbonyl compound could be detected.

The epoxide, heated with aqueous-alcoholic 30% sulphuric acid containing 2 : 4-dinitrophenylhydrazine, gives the 2-*tert.*-butyl-2 : 4 : 4-trimethylpentanal 2 : 4-dinitrophenylhydrazone (not very good yield) as yellow needles, m. p. and mixed m. p. 152—153°.

2 : 2 : 4-*Trimethylhex*-3-*ene*.—The crude stearate of 2 : 2 : 4-trimethylhexan-3-ol [from the alcohol (72 g.) and stearoyl chloride (from 150 g. of stearic acid)] was heated at 360° for 4 hr. with pyridine (2 c.c.). The olefin, obtained in 56% yield, had b. p. 128°, n_D^{20} 1·4230. It was identified by ozonolysis to trimethylacetaldehyde and ethyl methyl ketone. No other carbonyl compound could be detected. When the stearate was pyrolysed without the addition of pyridine, the olefin had b. p. 128—132°, n_D^{20} 1·4226—1·4248. Whitmore and Laughlin[6]

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[5] Whitmore *et al.*, *J. Amer. Chem. Soc.*, 1937, **59**, 643.

[6] Whitmore and Laughlin, *ibid.*, 1933, **55**, 3737.

dehydrated 2 : 2 : 4-trimethylhexan-3-ol by heating it with naphthalene-2-sulphonic acid and obtained mixed 2 : 2 : 4-trimethylhex-3- and -4-ene, b. p. 128—130·2°, n_D^{20} 1·4220.

The olefin with benzoyl hydrogen peroxide in chloroform gives 3 : 4-*epoxy*-2 : 2 : 4-*trimethylhexane* (45%), b. p. 80—80·5°/77 mm., n_D^{20} 1·4170—1·4165 (Found : C, 75·8; H, 12·8. $C_9H_{18}O$ requires C, 76·0; H, 12·6%). There was also formed some higher-boiling material which could not be isolated in a pure state. The epoxide is reduced by lithium aluminium hydride in ether to 2 : 2 : 4-trimethylhexan-3-ol (3 : 5-dinitrobenzoate, m. p. and mixed m. p. 88—90°).

The epoxide (1 g.), shaken for 16 hr. with 0·5% sulphuric acid (5 c.c.), gave the glycol (0·4 g.), b. p. 108—110°/23 mm., with low-boiling material. Oxidative fission of the glycol with aqueous-alcoholic periodic acid gave ethyl methyl ketone and trimethylacetaldehyde.

Rearrangement of the epoxide by 30—50% aqueous sulphuric acid containing 2 : 4-dinitrophenylhydrazine gave two products both in poor yield: (*a*) orange needles (m. p. 146—146·5° (Found : C, 56·4; H, 6·8; N, 17·1. $C_{15}H_{22}O_4N_4$ requires C, 55·9; H, 6·9; N, 17·4%); and (*b*) bright yellow needles, m. p. 138°, in amount insufficient for analysis. The latter were also formed by using 90% phosphoric acid and a solution of the epoxide in light petroleum.

4-*Ethyl*-2 : 2-*dimethylhex*-3-*ene*.—This was obtained in 62% yield by heating the stearate of 4-ethyl-2 : 2-dimethylhexan-3-ol at 380° after the addition of some pyridines; it had b. p. 147°, n_D^{20} 1·4297, and gave only trimethylacetaldehyde and diethyl ketone on ozonolysis. 3 : 4-*Epoxy*-4-*ethyl*-2 : 2-*dimethylhexane*, b. p. 54—55°/12 mm., n_D^{20} 1·4243 (Found : C, 77·2; H, 12·7. $C_{10}H_{20}O$ requires C, 76·9; H, 12·9%), when heated to the b. p. with aqueous-alcoholic 50% sulphuric acid containing some 2 : 4-dinitrophenylhydrazine gave an oil from which a small amount of a yellow 2 : 4-dinitrophenylhydrazone separated in yellow needles, m. p. 131°, (from light petroleum), probably the dinitrophenylhydrazone of 2 : 2-diethyl-3 : 3-dimethylbutanal.

Hydration of the epoxide by 0·1N-sulphuric acid gave after 17 hr. only a poor yield of a glycol (0·18 g.), with volatile products. The glycol was oxidised by aqueous periodic acid, to diethyl ketone and trimethylacetaldehyde.

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