71. *Reactions of Unsaturated Compounds. Part V. The Action of Organic Peracids on* β-*Diisobutylene* (2 : 4 : 4-*Trimethylpent*-2-*ene*).

By A. Byers and W. J. Hickinbottom.

β-Di*iso*butylene (2 : 4 : 4-trimethylpent-2-ene) reacts with perbenzoic, peracetic, and performic acids to give smaller or larger amounts of an unsaturated alcohol in addition to the normal product.

With perbenzoic acid in chloroform solution, the main product is 2 : 3-*epoxy*-2 : 4 : 4-*trimethylpentane* ; the yield of unsaturated *alcohol* is small.

An acetic acid solution of peracetic acid reacts to yield, after alkaline hydrolysis, 2 : 4 : 4-*trimethylpentane*-2 : 3-*diol* and 2 : 4 : 4-*trimethylpent*-1-*en*-3-*ol* in approximately equal amounts. A third product is an apparently homogeneous oil, b. p. 145—151°/25 mm., having the molecular formula $C_{16}H_{32}O_3$. It yields at least two isomeric crystalline *mono*-p-*nitrobenzoates* and by acid hydrolysis is split into C_8 residues. These reactions suggest that the oil is a mixture of isomeric monohydroxy-compounds, each containing two ether linkages. Probable structures are discussed.

Performic acid in excess of formic acid reacts with β-di*iso*butylene in a similar manner, except that the yield of glycol is considerably greater. There is evidence also of the formation of a diether of the formula $C_{16}H_{32}O_2$.

Perbenzoic acid is a recognised reagent for the preparation of epoxides directly from olefins (Prileschajew, *Ber.*, 1909, **42**, 4811; *J. Russ. Phys. Chem. Soc.*, 1911, **42**, 1387; Böeseken and Blumberger, *Rec. Trav. chim.*, 1925, **44**, 90; Nametkin and Brüssoff, *J. pr. Chem.*, 1926, **112**, 169; Meerwein, *ibid.*, 1926, **113**, 9). There appears to be no well-authenticated example of this reaction proceeding other than with the formation of the epoxide, although Meerwein (*loc. cit.*) has reported an abnormal consumption by unsymmetrically substituted olefins. No abnormal products were isolated or identified. Bradsher (*J. Amer. Chem. Soc.*, 1944, **66**, 45), however, has described a dioxide $C_{20}H_{16}O_2$ from 1 : 1 : 2-triphenylethylene, but its structure is still uncertain.

In the present paper it is found that perbenzoic acid reacts with β-di*iso*butylene (2 : 4 : 4-trimethylpent-2-ene) (I) to form the corresponding epoxide (II). The product, however, is not homogeneous; there is a noticeable amount of a compound isomeric with the epoxide, but differing from it in boiling point and refractive index, and also in being unsaturated. It yields an α-*naphthylurethane* and a p-*nitrobenzoate* which have been found to be identical with those from the unsaturated alcohol obtained by the action of peracetic acid on β-di*iso*butylene.

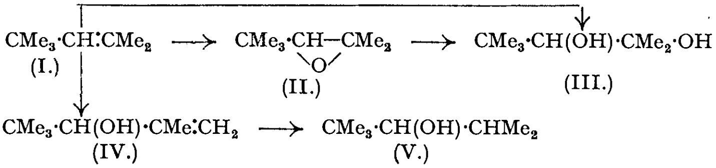
Peracetic acid in ethereal solution is reported to react with olefins to give the epoxide as the primary product (Arbusov and Michailov, *J. pr. Chem.*, 1927, **127**, 1, 92). If acetic acid is used as a solvent, the epoxide ring may be opened with the formation of a glycol and its esters (Böeseken *et al.*, *Rec. Trav. chim.*, 1926, **45**, 838; 1928, **47**, 683; 1929, **48**, 363; 1935, **54**, 657;

Arbusov and Michailov, *loc. cit.*). Some olefins are reported to behave abnormally in that poor yields of the glycol are obtained, together with resinous matter and other unidentified products (Böeseken and Elsen, *Rec. Trav. chim.*, 1929, **48**, 363; Arbusov and Michailov, *loc. cit.*). As far as the authors are aware, there is no record of any of the products of this reaction having been isolated, or of any reliable indication of their nature.

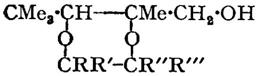
In the present paper, a study has been made of the behaviour of β-di*iso*butylene towards peracetic acid in acetic acid solution. Reaction occurs exothermally, and the product, after alkaline hydrolysis, contains not only the expected glycol but important amounts of an unsaturated alcohol (*A*) and a higher-boiling viscous oil (*B*). The yields of these three main products vary somewhat with the experimental conditions, but in general the glycol and the unsaturated alcohol are formed in approximately equal amounts (see p. 288); the yield of the oil (*B*) is generally somewhat lower.

The glycol is presumably identical with that isolated by Prileschajew (*Ber.*, 1909, **42**, 4811) from the hydrolysis of the mixed epoxides from a mixture of α- and β-di*iso*butylenes. It is now identified as 2 : 4 : *4-trimethylpentane-*2 : 3-*diol* (III) by oxidative fission to trimethylacetaldehyde, and by its independent preparation by oxidising β-di*iso*butylene with *tert.*-butyl hydrogen peroxide and osmium tetroxide. It was also obtained by hydrolysis of 2 : 3-epoxy-2 : 4 : 4-trimethylpentane (II).

The unsaturated alcohol (*A*) has the molecular formula $C_8H_{16}O$ and was purified through its crystalline p-*nitrobenzoate*. It was further characterised by its 3 : 5-*dinitrobenzoate* and its α-*naphthylurethane*. The unsaturated character of the alcohol was demonstrated by reaction with perbenzoic acid and hydrogenation to 2 : 4 : 4-trimethylpentan-3-ol (V). This identifies the unsaturated alcohol unambiguously as 2 : 4 : 4-*trimethylpent*-1-*en*-3-ol (IV). The formation of this alcohol from β-di*iso*butylene occurs with alteration in the position of the double bond. The mechanism of this reaction forms the subject of another paper.



The higher-boiling fraction (*B*) is an apparently homogeneous viscous oil, b. p. 145—151°/25 mm., of the molecular formula $C_{16}H_{32}O_3$. It reacts with *p*-nitrobenzoyl chloride in pyridine to yield a mixture of crystalline *p*-nitrobenzoates and a viscid oil. One ester has been obtained pure and is a *mono*-p-*nitrobenzoate*, $C_{16}H_{31}O_2(CO_2{\cdot}C_6H_4{\cdot}NO_2)$. The lower-melting fractions of the ester have the same composition. It is evident that fraction (*B*) consists of at least two isomers, each containing one free hydroxyl group. Evidence of the nature of one of the other oxygen atoms is provided by its hydrolysis with aqueous alcoholic sulphuric acid in presence of 2 : 4-dinitrophenylhydrazine. A *dihydropyrazole*, $C_{14}H_{18}O_4N_4$, is formed identical with that from 1 : 2-epoxy-2 : 4 : 4-trimethylpentan-3-ol, showing that fission has occurred to a C_8 residue. The simplest and also the most probable explanation of this observation is that the compound $C_{16}H_{32}O_3$ is an ether in which two C_8 residues are joined together by at least one oxygen. In arriving at this conclusion due consideration has been given to the possibility that $C_{16}H_{32}O_3$ has a tetra*iso*butylene structure, which may also break down under the influence of fairly concentrated acid. But it seems likely that the degradation of such a structure would not yield such simple products as have been obtained. Moreover the tetra*iso*butylene structure does not fit in well with some more recent and unpublished observations on analogous products. If the compound $C_{16}H_{32}O_3$ is then formulated as $HO{\cdot}C_8H_{15}{\cdot}O{\cdot}C_8H_{16}O$, the disposition of the third oxygen as a second ether linkage is indicated. This leads to the formulation of the compound as either a hydroxy-substituted dioxan (VI, VII, VIII) or an epoxyhydroxy-ether (IX).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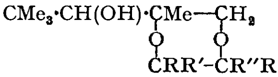
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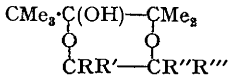
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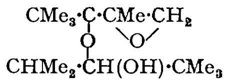
(IX.)

(R, R′, R″, R‴ = CMe_3, Me, H.)

Of these, the dioxan structure is considered to be the more probable.

The use of performic acid for the hydroxylation of olefins has recently been developed by Swern, Billen, Findley, and Scanlan (*J. Amer. Chem. Soc.*, 1945, **67**, 1786), and Swern, Billen, and Scanlan (*ibid.*, 1946, **68**, 1504). In this procedure, the performic acid is prepared in presence of the olefin by adding hydrogen peroxide (30%) to a solution of the olefin in anhydrous formic acid. The authors claim that no products other than the monoformic ester of the glycol are obtained. It is found that β-di*iso*butylene reacts with hydrogen peroxide in formic acid to yield a product which after alkaline hydrolysis does consist largely of the expected glycol. There is formed in addition 2 : 4 : 4-trimethylpent-1-en-3-ol and higher boiling material, which is presumably substituted dioxan. The yield of these by-products is much smaller than that from peracetic acid, but if the observations of Swern *et al.* are to be accepted, β-di*iso*butylene is an exception among other olefins in yielding by-products when acted upon by performic acid.

EXPERIMENTAL.

(Analyses are by Drs. Weiler and Strauss, Oxford. B. ps. are uncorrected unless the contrary is stated.)

β-Di*iso*butylene (2 : 4 : 4-trimethylpent-2-ene) was obtained from Imperial Chemical Industries Ltd. (Billingham Division), and was substantially pure, b. p. 104·1°/748 mm. (corr.), $n_D^{20°}$ 1·4160. The position of the double bond was confirmed by ozonolysis to trimethylacetaldehyde (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 208°; semicarbazone, m. p. and mixed m. p. 190°).

Oxidation by *tert.*-butyl hydrogen peroxide in *tert.*-butyl alcohol with osmium tetroxide as catalyst (Milas and Sussman, *J. Amer. Chem. Soc.*, 1936, **58**, 1302) gave trimethylacetaldehyde and 2 : 4 : 4-*trimethylpentane*-2 : 3-*diol*, prismatic needles from light petroleum (b. p. 40—60°), m. p. 65—66° (Found : C, 65·6; H, 12·3. $C_8H_{18}O_2$ requires C, 65·7; H, 12·5%).

Reaction with *p*-nitrobenzoyl chloride in pyridine yielded an ester, forming stellate groups of needles from light petroleum (b. p. 40—60°), m. p. 77—78°, which was probably the *mononitrobenzoate* (Found : C, 60·5; H, 7·2. $C_{15}H_{21}O_5N$ requires C, 61·0; H, 7·1%).

Oxidation of the glycol by lead tetra-acetate in acetic acid or by aqueous-alcoholic periodic acid gave trimethylacetaldehyde (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 208°; semicarbazone, m. p. and mixed m. p. 190°).

2 : 4 : 4-Trimethylpentane-2 : 3-diol on being heated with 2 : 4-dinitrophenylhydrazine in 50% aqueous-alcoholic sulphuric acid presumably underwent a pinacolin rearrangement to give the 2 : 2 : 3 : 3-*tetramethylbutanal* 2 : 4-*dinitrophenylhydrazone*, golden yellow felted needles from alcohol–pyridine, m. p. 163—164° (Found : C, 54·7; H, 6·5; N, 17·9. $C_{14}H_{20}O_4N_4$ requires C, 54·5; H, 6·5; N, 18·2%).

*Reaction of β-Di*iso*butylene with Perbenzoic Acid.*—Freshly distilled β-di*iso*butylene (50 c.c.) and a dry chloroform solution of perbenzoic acid (30 g.) were mixed and kept at room temperature in the dark until all the peracid had disappeared. The solution was then shaken successively with aqueous sodium carbonate and water, before being dried and distilled. 2 : 3-*Epoxy*-2 : 4 : 4-*trimethylpentane* (26·4 g.) was collected in an approximately pure state between 120° and 135°, $n_D^{20°}$ 1·4117, with a small amount of a fraction (1·15 g.) at 150—160°, $n_D^{20°}$ 1·4350. The pure epoxide boils at 130—131° (corr.), $n_D^{20°}$ 1·4092 (Found : C, 74·7; H, 12·5. $C_8H_{16}O$ requires C, 74·9; H, 12·6%); it is a clear mobile liquid with an odour reminiscent of the parent olefin, and is stable to N/100-aqueous permanganate over a period of at least 2 hours. It is very slowly hydrolysed by cold water, somewhat more rapidly by boiling with water or by cold dilute sulphuric acid, to yield 2 : 4 : 4-trimethylpentane-2 : 3-diol.

The fraction, b. p. 150—160°, was unsaturated and reacted with α-naphthyl *iso*cyanate to yield, among other products, the α-naphthylurethane of an unsaturated alcohol, identical with that derived from the reaction of peracetic acid. The identity was confirmed by the preparation of the *p*-nitrobenzoate and its comparison with an authentic specimen.

The unsaturated alcohol isolated in an approximately pure state was less than 1% of the total oxidation product.

*Reaction of β-Di*iso*butylene with Peracetic Acid.*—(a) *Preparation of peracetic acid.* An approximately M-solution of peracetic acid was prepared by adding 450 c.c. of acetic anhydride containing 4·5 g. of sulphuric acid to 90 c.c. of commercial 30% hydrogen peroxide. Efficient stirring and a cooling bath are both necessary, as well as a controlled addition of the acetic anhydride, in order to maintain a temperature of 20—25° in the mixture. About 4—5 hours are required for the addition, and after a further period of 1 hour only small amounts of hydrogen peroxide were present. In the work described in this paper, the solution was kept for at least 12 hours until all the hydrogen peroxide had disappeared. The solution then contained approximately 60—65 g. of peracetic acid as determined by Smit's method (*Rec. Trav. chim.*, 1930, **49**, 675). It was used for the oxidations described in this paper, either (i) as prepared and containing free sulphuric acid, or (ii) after being stirred with 10 g. of finely powdered anhydrous sodium acetate to remove the free mineral acid.

This method of preparation is essentially that described by Findley, Swern, and Scanlan (*J. Amer. Chem. Soc.*, 1945, **67**, 412), which is a modification of Smit's method (*loc. cit.*, p. 691). A temperature of 40° during the reaction, as recommended by Findley *et al.*, is unnecessary.

(b) *Reaction with peracetic acid.* The following general conditions were used. Freshly distilled olefin (1·1 mols.) was added slowly to the solution of the peracid (1 mol.). Reaction occurs exothermally, and efficient cooling and stirring are necessary to maintain a temperature of 20—30° during the addition. The mixture was kept overnight or until all the peracid had gone; it was then neutralised by adding a solution of 400 g. of sodium hydroxide in 800 c.c. of water. An oil separated and was stirred with the alkaline solution until neutral.

The upper layer was then removed and combined with the etheral extracts of the lower alkaline layer. After removal of the volatile solvent, the product was heated under reflux for 2—3 hours with a solution of 50 g. of potassium hydroxide in 100 c.c. of 50% aqueous methyl alcohol to hydrolyse any esters which might have been present. The product was isolated by dilution with water and extraction with ether. The dried ethereal extract was freed from solvent, and the residue distilled under reduced pressure. This preliminary distillation gave three main fractions: (*A*) b. p. <90°/30 mm., (*B*) b. p. 90—120°/30 mm., (*C*) b. p. 130—150°/30 mm.

(c) *Identification of the products.* The fraction (*A*) was distilled through a short column packed with glass helices. The following gives a typical separation, any unchanged olefin being neglected: 130—145°, 1·10 g., $n_{\mathrm{D}}^{20^\circ}$ 1·4115; 145—150°, 2·4 g., $n_{\mathrm{D}}^{20^\circ}$ 1·4242; 150—160°, 9·4 g., $n_{\mathrm{D}}^{20^\circ}$ 1·4334; 160—175°, 3·3 g., $n_{\mathrm{D}}^{20^\circ}$ 1·4363; 175—185°, 1·3 g., $n_{\mathrm{D}}^{20^\circ}$ 1·4353; the residue (2·25 g.) solidified on cooling and consisted chiefly of 2 : 4 : 4-trimethylpentane-2 : 3-diol. Further fractionation concentrated the greater part of the product in the fraction 150—160°, with smaller amounts at 130—145° and 170—180°.

(d) *Isolation of* 2 : 4 : 4-*trimethylpent*-1-*en*-3-*ol.* Preliminary examination showed that the fraction b. p. 150—160° was unsaturated and was essentially an alcohol. It was converted, by reaction with *p*-nitrobenzoyl chloride in pyridine, into a crystalline p-*nitrobenzoate*, very pale yellow plates from alcohol, m. p. 79—80° (Found: C, 64·75; H, 6·85; N, 5·2. $C_{15}H_{19}O_4N$ requires C, 64·95; H, 6·9; N, 5·05%).

Hydrolysis of the pure *p*-nitrobenzoate with aqueous-alcoholic alkali gave pure 2 : 4 : 4-*trimethylpent*-1-*en*-3-*ol*, b. p. 154·8—155·0° (corr.)/753 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4372 (Found: C, 74·7, 74·6; H, 12·65, 12·55. $C_8H_{16}O$ requires C, 74·9; H, 12·6%).

It was characterised by its 3 : 5-*dinitrobenzoate*, platelets from alcohol, m. p. 123° (Found: C, 55·8; H, 5·8; N, 8·9. $C_{15}H_{18}O_6N_2$ requires C, 55·7; H, 5·9; N, 8·7%), and its α-*naphthylurethane*, needles from light petroleum (b. p. 60—80°), m. p. 137° (Found: C, 76·6; H, 7·7. $C_{19}H_{23}O_2N$ requires C, 76·7; H, 7·8%).

Hydrogenation of the unsaturated alcohol in absolute alcohol (PtO_2) gave 2 : 4 : 4-trimethylpentan-3-ol, b. p. 151—152° (corr.), $n_{\mathrm{D}}^{20^\circ}$ 1·4287; α-*naphthylurethane*, spherical aggregates of small needles from light petroleum (b. p. 60—80°), m. p. 110° alone or admixed with a genuine specimen (Found: C, 76·7; H, 7·8. $C_{19}H_{25}O_2N$ requires C, 76·3; H, 7·7%). The identification was further confirmed by oxidation of the reduced alcohol to pentamethylacetone; 2 : 4-*dinitrophenylhydrazone*, orange-red laminæ, m. p. and mixed m. p. 163—164° (Found: C, 54·55; H, 6·4; N, 18·2. $C_{14}H_{20}O_4N_4$ requires C, 54·5; H, 6·5; N, 18·2%).

(e) *Identification of* 1 : 2-*epoxy*-2 : 4 : 4-*trimethylpentan*-3-*ol.* The fraction b. p. 175—185°, after further distillations, gave a colourless oil, b. p. 180—185°, which was only approximately pure. An alcoholic solution reacted with a hot solution of 2 : 4-dinitrophenylhydrazine in 50% sulphuric acid to give bright red needles from glacial acetic acid, m. p. 204°.

For comparison, 1 : 2-*epoxytrimethylpentan*-3-*ol* was prepared by interaction of 2 : 4 : 4-trimethylpent-en-3-ol and perbenzoic acid in chloroform. After the usual treatment to remove free acid and excess of solvent, the approximately pure epoxide was collected at 80—83/25 mm. as a colourless oil, $n_{\mathrm{D}}^{20^\circ}$ 1·4407, which solidified on cooling, m. p. 28—29° after draining on porous earthenware (Found: C, 67·1; H, 11·4. $C_8H_{16}O_2$ requires C, 66·7; H, 11·2%). It reacted with 2 : 4-dinitrophenylhydrazine to yield a *compound*, m. p. 204°, identical with that obtained as previously described (Found: C, 55·0; H, 6·0; N, 18·1. $C_{14}H_{18}O_4N_4$ requires C, 54·9; H, 5·9; N, 18·3%). This compound is probably a 2 : 4-*dinitrophenylpyrazoline* having methyl and *tert.*-butyl substituents, the orientation of which is uncertain owing to the possibility of isomerisation during the preparation.

(f) *Isolation of* 2 : 4 : 4-*Trimethylpentane*-2 : 3-*diol.* The fraction (*B*) (see above), b. p. 90—120°/30 mm., solidified on cooling, and by draining and crystallisation from light petroleum (b. p. 40—60°) the pure glycol was obtained, m. p. and mixed m. p. 65—66°.

(g) *Isolation of a monohydroxy-diether.* The high-boiling fraction (*C*) was distilled under reduced pressure after a further hydrolysis. The following is a typical preliminary separation: 100—120°/27 mm., 1·8 g., $n_{\mathrm{D}}^{20^\circ}$ 1·4452 (deposited glycol on cooling); 120—135°/26 mm., 0·5 g., $n_{\mathrm{D}}^{20^\circ}$ 1·4465; 135—145°/25 mm., 0·95 g., $n_{\mathrm{D}}^{20^\circ}$ 1·4482; 145—151°/25 mm., 10·5 g., $n_{\mathrm{D}}^{20^\circ}$ 1·4494. Two further distillations of the last fraction separated some lower-boiling material and gave a main fraction, b. p. 144—146°/22 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4509. This on further distillation appeared to be homogeneous as judged by the refractive indexes of each successive fraction. The *substance* was a clear viscous liquid which is stable to N/100-permanganate for at least ½ hour [Found (specimens from two different preparations): C, 70·5, 75·0; H, 11·85, 12·0. $C_{16}H_{32}O_3$ requires C, 70·5; H, 11·9%].

On being heated with 2 : 4-dinitrophenylhydrazine in aqueous-alcoholic sulphuric acid (50%), it yielded a paste of crystals from which a red substance was obtained, needles from glacial acetic acid or ethyl acetate, m. p. 204°. This was identical in every respect with the pyrazoline obtained by a similar method from 1 : 2-epoxy-2 : 4 : 4-trimethylpentan-3-ol.

Reaction with *p*-nitrobenzoyl chloride in pyridine gave a semi-solid product which was separated by means of alcohol into a viscid syrup (*A*) and a crystalline product (*B*). Fractional crystallisation of (*B*), first from alcohol and then from light petroleum, gave a pure *mono*-p-*nitrobenzoate*, slender needles from light petroleum, m. p. 126° (Found: C, 65·4, 65·5; H, 8·3, 8·1; N, 2·9. $C_{23}H_{35}O_6N$ requires C, 65·5; H, 8·4; N, 3·3%). No complete separation of a second substance was achieved. An analysis of the crystalline material, m. p. 96—98°, from the most soluble fraction gave the same results as for the pure ester (Found: C, 65·4; H, 8·2%).

The viscid syrup (*A*) was partially resolved by chromatographic adsorption on alumina into more crystalline material. The less strongly adsorbed material was hydrolysed with aqueous-alcoholic alkali to yield *p*-nitrobenzoic acid and an oil, b. p. 141—143°/19 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4501, having a composition approximating to that of the original material (Found: C, 71·1; H, 11·5. $C_{16}H_{32}O_3$ requires C, 70·5; H, 11·9%). By reaction with 2 : 4-dinitrophenylhydrazine it gave a pyrazoline identical with the original material.

The following table summarises the yields obtained in some of these preparations.

Reactants (g.).			Products (g.).		
Peracetic acid.	β-Di*iso*-butylene.	Other substances.	Crude unsat. alc., b. p. 145—160°.	Glycol, m. p. 65—66°.	B. p. 130—150°/25 mm.
46	80	Sulphuric acid (3 g.)	15·1	14·9	10·5
65	96	Sulphuric acid (4 g.)	26	24	19
91	126	Sulphuric acid (4·5 g.)	30·4	?	5·4
75	120	Sodium acetate (10 g.)	23	35·5	12

Reaction with Performic Acid.—The method for the preparation of performic acid described by Swern, Billen, Findley, and Scanlan (*J. Amer. Chem Soc.*, 1945, **67**, 1786) was used.

Concentrated hydrogen peroxide (140 c.c., 30%) was added slowly and regularly to an efficiently stirred solution of freshly distilled β-di*iso*butylene (120 g.) in 500 g. of anhydrous formic acid (commerial, 98—100%). The reaction is exothermic, and the temperature was kept below 35° by an external bath of running water. The addition required 2 hours and the reaction was completed by keeping the mixture for 18 hours at room temperature.

The product was isolated by neutralising the formic acid with 50% aqueous sodium hydroxide. The oil which separated was removed with the aid of ether and then heated with aqueous-alcoholic sodium hydroxide to hydrolyse any formic esters that might have been formed.

The hydrolysis solution was diluted with water and extracted several times with ether. The dried extracts, after removal of solvent, left a viscous syrup which solidified on cooling. Trituration with cold light petroleum (b. p. 40—60°) left pure 2 : 4 : 4-trimethylpentane-2 : 3-diol as a white crystalline mass, m. p. 65—66.°

The light petroleum extracts were separated by distillation into three main fractions: (*a*) b. p. 110—175°, (*b*) 2 : 4 : 4-trimethylpentane-2 : 3-diol, b. p. 100—110°/25 mm., (*c*) b. p. 110—150°/20 mm.

Examination of fraction (a).

A preliminary distillation gave the following fractions: 110—130°, 0·60 g., $n_D^{20^\circ}$ 1·4148; 130—143°, 0·85 g., $n_D^{20^\circ}$ 1·4180 (solid separated); 143—153°, 3·65 g., $n_D^{20^\circ}$ 1·4221 (solid separated); 153—163°, 2·60 g., $n_D^{20^\circ}$ 1·4249; 163—173°, 0·75 g., $n_D^{20^\circ}$ 1·4259; 173—175°, 0·90 g., $n_D^{20^\circ}$ 1·4256. The residue on fractionation under reduced pressure gave some glycol.

The refractive index of the lower-boiling fractions suggests the presence of epoxide. They were mixed with aqueous alcohol and kept for 3 weeks at room temperature. On redistillation the fractions up to 145° partly solidified. The higher-boiling fractions, b. p. 145—165°, had $n_D^{20^\circ}$ 1·4242—1·4251, and were unsaturated and alcoholic. From these a 3 : 5-dinitrobenzoate, m. p. 123°, was obtained, identical with that of 2 : 4 : 4-trimethylpent-1-en-3-ol. There was also present a second dinitrobenzoate which could not be isolated in a pure state.

Examination of fraction (c).

Fractional distillation gave the following results: $<$100°/25 mm., 4·5 g. (chiefly glycol); 100—120°/25 mm., 0·95 g.; 120—135°/25 mm., 0·40 g.; 135—143°/25 mm., 3·70 g., n_D 1·4456.

The last fraction, on being heated with 2 : 4-dinitrophenylhydrazine in aqueous alcoholic 50% sulphuric acid, gave a yellow dinitrophenylhydrazone not identified and the red pyrazoline, m. p. 204°, previously obtained from 1 : 2-epoxy-2 : 4 : 4-trimethylpentan-3-ol.

In this preparation a total of 67·6 g. of 2 : 4 : 4-trimethylpentane-1 : 2-diol was obtained with 3·7 g. of high boiling product and 6·25 g. of low-boiling alcohols, chiefly 2 : 4 : 4-trimethylpent-1-en-3-ol.

A second preparation using β-di*iso*butylene (73 g.), hydrogen peroxide (80 c.c., 30%), and formic acid (300 c.c.), gave 39·4 g. of pure glycol, 5·95 g. of low-boiling alcohols, b. p. 143—163°, and 3·0 g. of high-boiling product, b. p. 135—143°/25 mm.

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