264. *Reactions of Unsaturated Compounds. Part VI. The Reaction of α-Diïsobutylene with Organic Per-acids.*

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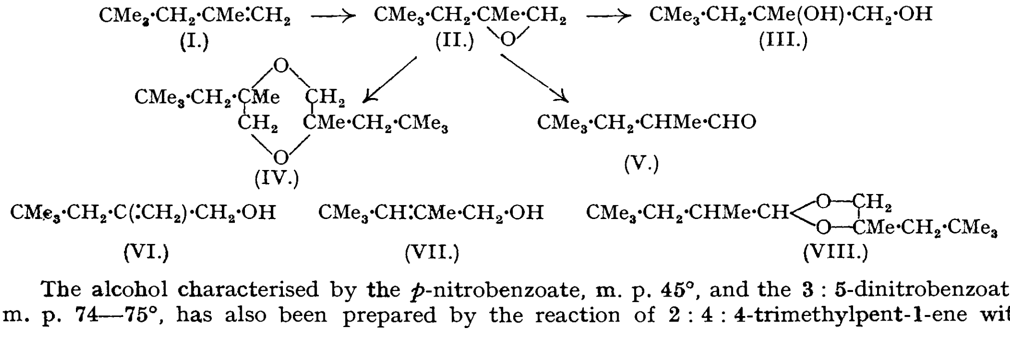
2 : 4 : 4-Trimethylpent-1-ene reacts with perbenzoic acid in chloroform to give 1 : 2-*epoxy*-2 : 4 : 4-*trimethylpentane.* With performic acid in an excess of formic acid, the epoxide is obtained with 2 : 4 : 4-*trimethylpentane*-1 : 2-*diol* as the main products; 2 : 2-dimethylpentan-4-one, 2 : 4 : 4-trimethylpentanal, and a diether, provisionally formulated as 2 : 5-*dimethyl*-2 : 5-*di*neo*pentyl*-1 : 4-*dioxan,* have also been isolated. The yields of aldehyde and dioxan are increased at the expense of the glycol if the reaction temperature rises unduly.

On using peracetic acid in acetic acid–acetic anhydride solution, the same products are formed as with performic acid; in addition, two unsaturated alcohols are formed—4 : 4-dimethyl-2-hydroxymethylpent-1-ene and 2 : 4 : 4-trimethylpent-2-en-1-ol, each of which has been characterised by its 3 : 5-*dinitrobenzoate.*

The reaction between 2 : 4 : 4-trimethylpent-1-ene (I) and perbenzoic acid in chloroform gives the normal product 1 : 2-*epoxy*-2 : 4 : 4-*trimethylpentane* (II). With performic or peracetic acid the reaction is more complex. The product from either reaction contains the epoxide (II) together with 2 : 4 : 4-*trimethylpentane*-1 : 2-*diol* (III), and a *diether* (IV). As minor products 2 : 2-dimethylpentan-4-one and 2 : 4 : 4-trimethylpentanal (V) are also present. There is also formed a viscous material of relatively high boiling point from which no homogeneous substance has yet been isolated and which may consist wholly or in part of polymerised unsaturated alcohols.

When peracetic acid was used the product also contained a mixture of unsaturated alcohols, which could be hydrogenated to 2 : 4 : 4-trimethylpentan-1-ol. This shows that the essential components of the mixture could not be other than (VI) and the *cis*- and *trans*-forms of (VII). From this mixture one component was isolated relatively easily as a p-*nitrobenzoate,* m. p. 45°, and a 3 : 5-*dinitrobenzoate,* m. p. 74—75°, but considerable difficulty was encountered in obtaining any of the other components in a pure state; a small amount of a 3 : 5-*dinitrobenzoate,* m. p. 51°, has been obtained and is probably homogeneous.



The alcohol characterised by the *p*-nitrobenzoate, m. p. 45°, and the 3 : 5-dinitrobenzoate, m. p. 74—75°, has also been prepared by the reaction of 2 : 4 : 4-trimethylpent-1-ene with selenium dioxide, and it is provisionally assigned the structure (VI). The alcohol obtained from 2 : 4 : 4-trimethylpent-2-ene by reaction with selenium dioxide and characterised by its *p*-nitrobenzoate, m. p. 55—56°, and 3 : 5-dinitrobenzoate, m. p. 80° (this vol., p. **1333**), is provisionally considered to be either the *cis*- or the *trans*-form of (VII).

The diether (IV) has the molecular formula $C_{16}H_{32}O_2$. It is not appreciably attacked by cold dilute aqueous permanganate, does not react with *p*-nitrobenzoyl chloride, and is stable to hot aqueous sodium hydroxide. On hydrolysis with hot aqueous alcoholic sulphuric acid containing 2 : 4-dinitrophenylhydrazine, the 2 : 4-*dinitrophenylhydrazone* of 2 : 4 : 4-trimethylpentanal (V) is formed. These reactions admit of two possible types of structure, (IV) and (VIII). Of these (IV) is preferred since it is formed from the epoxide in presence of an excess of diluted aqueous sulphuric acid, and the yield is increased at the expense of the glycol if the temperature is allowed to rise (see following paper).

EXPERIMENTAL.

(Analyses by Drs. Weiler and Strauss, Oxford. All b. p.s are uncorrected unless recorded otherwise.)

2 : 4 : 4-Trimethylpent-1-ene (α-di*iso*butylene) was supplied by I.C.I. Ltd. (Billingham Division) and was substantially pure; b. p. 101·5°, $n_{\mathrm{D}}^{20^\circ}$ 1·4089. In all the experiments now recorded in this paper, it was freshly distilled over sodium immediately before use.

The position of the double bond was confirmed by oxidation with *tert.*-butyl hydrogen peroxide and osmium tetroxide (Milas and Sussman, *J. Amer. Chem. Soc.*, 1936, **58**, 1302; 1937, **59**, 2345) to give formaldehyde (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 163°; dimedone, m. p. and mixed m. p. 188—189°), 2 : 2-dimethylpentan-4-one (semicarbazone, m. p. and mixed m. p. 176°), and 2 : 4 : 4-*trimethylpentane*-1 : 2-*diol*, prisms or lozenge-shaped plates from light petroleum (b. p. 40—60°), m. p. 62—63° (Found : C, 65·7; H, 12·5. $C_8H_{18}O_2$ requires C, 65·7; H, 12·4%). The structure of the glycol was confirmed by oxidative fission with lead tetra-acetate in acetic acid solution to 2 : 2-dimethylpentan-4-one, b. p. 124·1—124·5°, $n_{\mathrm{D}}^{20^\circ}$ 1·4030, semicarbazone, m. p. and mixed m. p. 176°. Formaldehyde was also obtained and identified by its dimedone derivative, m. p. and mixed m. p. 189—190°.

The glycol undergoes intramolecular rearrangement on warming with diluted sulphuric acid to give, among other products, 2 : 4 : 4-trimethylpentan-1-al. This rearrangement is best demonstrated by warming with a 50% aqueous-alcoholic solution of sulphuric acid containing 2 : 4-dinitrophenyl hydrazine : a crystalline paste is obtained of 2 : 4 : 4-*trimethylpentanal* 2 : 4-*dinitrophenylhydrazone*, bright yellow needles, m. p. 143—144°, from acetic acid or ethyl acetate (Found : C, 54·3; H, 6·7; N, 17·9. $C_{14}H_{20}O_4N_4$ requires C, 54·5; H, 6·5; N, 18·2%).

(i) *Reaction with Perbenzoic Acid : Formation of* 1 : 2-*Epoxy*-2 : 4 : 4-*trimethylpentane*.—α-Di*iso*butylene (14 g.) was added to the equivalent amount of perbenzoic acid in chloroform. After several days' keeping at room temperature, the chloroform solution was shaken with successive amounts of aqueous sodium carbonate till free from benzoic acid. Distillation of the dried chloroform solution through an efficient colum gave the *epoxide* (6·5 g.), b. p. 140—141°/752 mm. (corr.), $n_{\mathrm{D}}^{20^\circ}$ 1·4157, as a colourless mobile liquid with a weak camphoraceous odour (Found : C, 75·1; H, 12·6. $C_8H_{16}O$ requires C, 74·9; H, 12·6%).

In contact with water at room temperature, the epoxide is slowly converted into 2 : 4 : 4-trimethylpentan-1 : 2-diol, m. p. and mixed m. p. 62—63°; about one-third had so reacted after 10 days. The hydrolysis occurs more rapidly on warming. The epoxide reacts with aqueous-alcoholic sulphuric acid containing 2 : 4-dinitrophenylhydrazine to yield the 2 : 4-dinitrophenylhydrazone of 2 : 4 : 4-trimethylpentan-1-al, m. p. and mixed m. p. 143—144°.

(ii) *Reaction with Performic Acid.*—Hydrogen peroxide (80 c.c., 100-vol.) was added all at once to a stirred solution of 2 : 4 : 4-trimethylpent-1-ene (100 c.c.) in 300 c.c. of commercial anhydrous formic acid (98—100%) at 20°. The temperature rose to 31° and reaction was controlled effectively by vigorous stirring and an external cooling bath of running water. After 2 days the reaction mixture was neutralised by the slow addition of 50% aqueous sodium hydroxide. The oil so obtained was removed and combined with the ethereal extracts of the aqueous layer. The ethereal solution was distilled under reduced pressure to collect all the distillate (A), b. p. up to 90°/30 mm. The residue was then hydrolysed with aqueous-alcoholic soda (B).

Isolation of products. (*a*) 1 : 2-Epoxy-2 : 4 : 4-trimethylpentane. The distillate (A) was fractionated through an efficient column, yielding the epoxide (6·95 g.), b. p. 140·5—141·5° (corr.), $n_{\mathrm{D}}^{20^\circ}$ 1·4175, identified by its conversion into the corresponding glycol by refluxing with aqueous alcohol for 36 hours. The fractions collected below 125—140° and 140° and 150°, when subjected to the same hydrolysis, gave further small amounts of glycol, together with 2 : 2-dimethylpentan-4-one, b. p. 120—125°, $n_{\mathrm{D}}^{20^\circ}$ 1·4040 (semicarbazone, m. p. and mixed m. p. 176°), 2 : 4 : 4-trimethylpentanal, b. p. 145—150° (identified by its semicarbazone, m. p. and mixed m. p. 119—120°), and 2 : 2-dimethylpentan-4-ol, b. p. 130—140° [3 : 5-*dinitrobenzoate*, m. p. and mixed m. p. 96° (Found : C, 54·3, 54·5; H, 6·0, 5·9; N, 8·8, 8·4. $C_{14}H_{18}O_6N_2$ requires C, 54·2; H, 5·85; N, 9·0%)].

(*b*) 2 : 4 : 4-Trimethylpentane-1 : 2-diol. The hydrolysed residue (B) generally crystallised after extraction from the alkaline layer and removal of the solvent. From it, pure glycol (18·6 g.) was isolated by crystallisation from light petroleum.

(*c*) 2 : 5-Dimethyl-2 : 5-di*neo*pentyl-1 : 4-dioxan. The mother-liquors from the crystallisation of the glycol gave on systematic fractionation further small amounts of glycol, and an apparently homogeneous, clear, viscous liquid, b. p. 128°/19 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4412 (Found : C, 75·3; H, 12·5. $C_{16}H_{32}O_2$ requires C, 74·9; H, 12·7%). This *compound* was stable to aqueous permanganate, was unchanged by refluxing with aqueous-alcoholic soda, and was recovered unchanged after successive treatment with *p*-nitro benzoyl chloride in pyridine and benzoyl chloride in pyridine; b. p. 128°/20 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4415 (Found : C, 74·8; H, 12·4%). On warming with 50% aqueous-alcoholic sulphuric acid containing 2 : 4-dinitrophenylhydrazine, it afforded the dinitrophenylhydrazone of 2 : 4 : 4-trimethylpentanal as the major product, m. p. and mixed m. p. 145° (Found : C, 54·3; H, 6·7; N, 17·9. Calc. : C, 54·5; H, 6·5; N, 18·2%).

In a second preparation the reaction mixture was not cooled and the temperature rose to 90°. On using α-di*iso*butylene (200 c.c.), formic acid (600 g.), and hydrogen peroxide (30%) (160 c.c.), the yield of glycol was 6·5 g.; of dioxan, 35·5 g.; 2 : 4 : 4-trimethylpentanal 13·75 g.; 2 : 2-dimethylpentan-4-one, 2·35 g.

The results of these and other preparations are summarised below.

		Yield of products, g.					
α-Di*iso*butylene, c.c.	Conditions, etc.	Glycol.	Unsat. alc.	Dioxan.	Me *neo*pentyl ketone.	Aldehyde.	Epoxide.
200	160 C.c. 30% H_2O_2, 600 g. formic acid; temp. <20°	17·75	—	2·95	+	+	+
200	160 C.c. 30% H_2O_2, 600 g. formic acid; temp. rose to 90°	6·5	—	35·5	2·35	13·75	—
100	80 C.c. 30% H_2O_2, 30 g. formic acid; temp. <30°	18·6	—	+	+	+	6·95
240	119 G. peracetic acid	16·35	1·5	18·1	0·65	—	0·5
280	125 G. peracetic acid	38·4	13	+	+	+	11
204	130 G. peracetic acid	44	+	8·7	—	—	14

(iii) *Reaction with Peracetic Acid.*—An acetic acid–acetic anhydride solution of peracetic acid was prepared as described in Part V (this vol., p. 286) and was used either (*a*) after adding an excess of fused sodium acetate to remove the free sulphuric acid, or (*b*) as prepared and containing the free sulphuric acid used as catalyst in the formation of the per-acid.

2 : 4 : 4-Trimethylpent-1-ene (280 c.c.) was added to a solution of peracetic acid which had been prepared from 200 c.c. of hydrogen peroxide (30%), 836 c.c. of acetic anhydride, and 7·8 c.c. of concentrated sulphuric acid. The solution contained 125 g. of peracetic acid and no free hydrogen peroxide. Before addition of the olefin, finely powdered anhydrous sodium acetate (30 g.) was stirred in. The temperature of the acid was kept below 25° by efficient stirring and cooling throughout the addition of the olefin, which required 5 hours. When the reaction was completed, the product was isolated and hydrolysed as described in Part V (*loc. cit.*). A preliminary distillation after removal of unchanged olefin gave three main fractions: (*a*) b. p. < 110°/25 mm., (*b*) 110—127°/25 mm., (*c*) > 127°/25 mm.

Isolation of products. (i) 2 : 4 : 4-Trimethylpentane-1 : 2-diol. The fraction (*b*) (b. p. 110—127°/25 mm.) solidified, and pure 2 : 4 : 4-trimethylpentane-1 : 2-diol, m. p. and mixed m. p. 62—63°, was obtained from it by crystallisation from light petroleum (b. p. 60—80°). Further amounts were obtained by fractional distillation of the mother-liquors and the residues from fraction (*a*) and the lower-boiling fractions from fraction (*c*). The total yield of glycol was 38·4 g.

(ii) 1 : 2-Epoxy-2 : 4 : 4-trimethylpentane, 4 : 4-dimethyl-2-hydroxymethylpent-1-ene, and 2 : 4 : 4-trimethylpent-2-en-1-ol. Distillation through a short packed column separated the distillate (*a*) (b. p. <110°/25 mm.) into two main fractions; (i) b. p. 130—145° (16·3 g.), $n_{\mathrm{D}}^{20^\circ}$ 1·4129—1·4147, and (ii) b. p. 175—200° (24—25 g.), $n_{\mathrm{D}}^{20^\circ}$ 1·4223—1·4332. Nothing homogeneous was isolated from the intermediate fractions (5·5 g.).

Fraction (i) consisted chiefly of 1 : 2-epoxy-2 : 4 : 4-trimethylpentane. It was isolated in a pure state by distillation, b. p. 139·5—141·5° (corr.), $n_{\mathrm{D}}^{20^\circ}$ 1·4152, and identified by hydrolysis to the corresponding glycol, m. p. and mixed m. p. 62—63°. This lower range also contained some 2 : 2-dimethylpentan-4-one which was isolated as semicarbazone, m. p. and mixed m. p. 176°, from the lower-boiling ranges of this fraction after removal of the epoxide by hydrolysis with aqueous alcohol.

The fraction (ii), b. p. 175—200°, after hydrolysis with aqueous-alcoholic alkali to ensure the absence of any esters, was distilled to give a main fraction between 170° and 185°, $n_{\mathrm{D}}^{20^\circ}$ 1·4333—1·4347. It was unsaturated and reacted with 3 : 5-dinitrobenzoyl chloride in pyridine to give a mixture of esters, which were separated with difficulty and considerable loss by crystallisation from light petroleum (b. p. 40—60°). From the sparingly soluble fractions, 4 : 4-*dimethyl*-2-*hydroxymethylpent*-1-*ene* 3 : 5-*dinitrobenzoate* was isolated, m. p. 74—75° (Found : C, 55·5; H, 6·2; N, 8·6. $C_{15}H_{18}O_6N_2$ requires C, 55·9; H, 5·6; N, 8·7%). This ester is identical with that of the unsaturated alcohol obtained by the oxidation of α-di*iso*butylene with selenium dioxide (this vol., p. 1333).

From the more soluble fractions a second *dinitrobenzoate* was isolated, m. p. 51°, sparingly soluble in cold alcohol (Found : C, 55·7; H, 6·0; N, 9·1. $C_{15}H_{18}O_6N_2$ requires C, 55·9; H, 5·6; N, 8·7%). The considerable loss attending the isolation of this compound did not permit an extended examination of this alcohol, which is considered provisionally to be 2 : 4 : 4-trimethylpent-2-en-1-ol.

(iii) 2 : 5-Dimethyl-2 : 5-di*neo*pentyl-1 : 4-dioxan. The distillate collected above 127°/25 mm. in the original separation was submitted to further fractionation. After the removal of some glycol, a fraction, b. p. 138—140°/33 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·4417, was obtained (5 g.). This has the characteristics of the dioxan isolated from the reaction of α-di*iso*butylene with performic acid (p. 1329). There was present also a considerable amount of higher-boiling material which was collected up to 180°/22 mm., leaving a dark viscous residue. Nothing homogeneous was obtained from these higher-boiling fractions, although an analysis of a fraction, b. p. 170—175°/27 mm., $n_D^{20°}$ 1·4480, gave figures corresponding with $C_{16}H_{32}O_2$ (Found : C, 74·7; H, 12·3. Calc. : C, 74·9; H, 12·7%).

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