

265. Reactions of Unsaturated Compounds. Part VII. The Mechanism of the Formation of Unsaturated Alcohols from Olefins by the Action of Organic Per-acids.

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2 : 3-Epoxy-2 : 4 : 4-trimethylpentane reacts with diluted sulphuric acid to give the corresponding glycol with notable amounts of 2 : 4 : 4-trimethylpent-1-en-3-ol, 2 : 2 : 5 : 5-tetramethyl-3 : 6-di-tert-butyl-1 : 4-dioxan, and a small amount of 2 : 2 : 3 : 3-tetramethylbutanal. The same products are formed by the action of a trace of sulphuric acid in acetic acid solution.

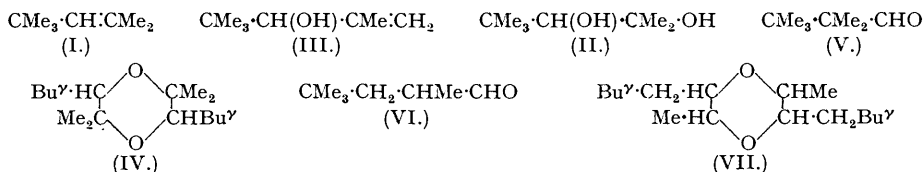
1 : 2-Epoxy-2 : 4 : 4-trimethylpentane with diluted sulphuric acid gives the corresponding glycol, with 2 : 5-dimethyl-2 : 5-dineopentyl-1 : 4-dioxan, 2 : 4 : 4-trimethylpentan-1-al, and a small amount of an unsaturated alcohol. If the temperature is allowed to rise during the reaction, the dioxan is formed at the expense of the glycol. There is sufficient qualitative agreement between the products of the reaction of α - and β -diisobutylenes with peracetic and performic acids and the hydration of the corresponding epoxides with aqueous sulphuric acid to justify the conclusion that the main cause of the formation of abnormal products by the reaction with per-acids is the abnormal behaviour of the epoxide.

A subsidiary cause of the formation of unsaturated alcohols when peracetic acid is used may be the elimination of the elements of acetic acid from the glycol diacetates either during the reaction or in the isolation of the products.

The reaction of both olefins with selenium dioxide has been examined. The results show quite clearly that the course of the formation of unsaturated alcohols by selenium dioxide does not depend on a preliminary saturation of the double bond.

2 : 4 : 4-TRIMETHYLPENT-2-ENE (I) reacts with peracetic acid in acetic acid-acetic anhydride solution to give the glycol (II) and its acetates with notable amounts of 2 : 4 : 4-trimethylpent-1-en-3-ol (III) and a hydroxy-diether. With performic acid the glycol is formed in greater amount, but the product still contains the unsaturated alcohol (III) and a diether which is provisionally formulated as 2 : 2 : 5 : 5-tetramethyl-3 : 6-di-tert-butyl-1 : 4-dioxan (IV) (Byers and Hickinbottom, this vol., p. 286).

This is the first identification of any of the abnormal products of the reaction of olefins with organic peracids and it seemed important that an inquiry should be made into the course and nature of the reactions which give rise to them.



The unsaturated alcohol (III) may be formed from the olefin by direct substitution, from the glycol (II) by dehydration, or from the epoxide by some reaction concurrent with hydration. Of these, the last seemed the more likely since the epoxide is the first and normal product of the action of organic per-acids on olefins. This has been established for perbenzoic acid (Prileschajew, *Ber.*, 1909, **42**, 481), perphthalic acid (Karrer and Jacker, *Helv. Chim. Acta*, 1945, **28**, 427, 471), peracetic acid (Arbusow and Michailow, *J. pr. Chem.*, 1930, **127**, 1, 92), and performic acid (Byers and Hickinbottom, this vol., p. 1328). The epoxide ring is opened by an excess of organic acid, such as acetic or formic, to give the corresponding glycol and its esters (Arbusow and Michailow, *loc. cit.*; Böeseken *et al.*, *Rec. Trav. chim.*, 1929, **48**, 363; 1935, **54**, 657).

It is now found that 2 : 3-epoxy-2 : 4 : 4-trimethylpentane (β -diisobutylene epoxide) behaves abnormally when treated in acetic acid with a trace of sulphuric acid or shaken with an excess of diluted sulphuric acid. The glycol (II) is formed together with 2 : 4 : 4-trimethylpent-1-en-3-ol (III), the diether (IV), and a small amount of 2 : 2 : 3 : 3-tetramethylbutanal (V). There is a sufficiently striking agreement between these products and those of the reaction of performic and peracetic acids on β -diisobutylene to support the contention that the reaction just described above is a phase of the reaction of the per-acids on the olefin.

This is strongly supported by the observation that 1 : 2-epoxy-2 : 4 : 4-trimethylpentane gives the same products when it is shaken with diluted sulphuric acid as does 2 : 4 : 4-trimethylpent-1-ene by reaction with performic or peracetic acid. This qualitative agreement is further demonstrated by the effect of an elevation of temperature on the reaction; the dioxan (VII) and 2 : 4 : 4-trimethylpentanal (VI) are obtained in greater yield at the expense of the glycol.

The literature contains surprisingly little information on the side reactions which accompany the hydration of an epoxide to the glycol. Methylene*cyclohexane* oxide (1 : 7-epoxymethylene*cyclohexane*) by the action of dilute sulphuric acid is reported to yield not only the glycol, but a dimer $C_{14}H_{22}O_2$ and an unsaturated alcohol, 1-hydroxymethylene*cyclohex-1-ene* (Kohler, Tischler, Potter, and Thompson, *J. Amer. Chem. Soc.*, 1939, **61**, 1059). 1 : 2-Epoxyphenylpropane gives hydrotropaldehyde and a dimer by the action of dilute aqueous acids or sodium hydrogen sulphite (Tiffeneau, *Ann. Chim.*, 1907, **10**, 176; Cohen, Marshall, and Woodman, *J.*, 1915, **107**, 898; Danilow and Venus-Danilowa, *Ber.*, 1927, **60**, 1059). Possibly there are other similar observations which have escaped our notice, but these recorded examples are sufficient to suggest that the hydration of an epoxide to a glycol is not a quantitative reaction in acid media. There are also some examples of the formation of unsaturated alcohols from epoxides by the action of dilute alkali (Bamberger and Lodter, *Annalen*, 1895, **288**, 100; Jorländer, *Ber.*, 1917, **50**, 1458). A discussion of the mechanism of the reaction is deferred till further experimental evidence has been accumulated.

Although the main course of the reaction seems sufficiently well established, it was nevertheless considered desirable to examine other possible causes of the formation of abnormal products, to ascertain how far they may have contributed to the general effect. The dehydration of the glycols by sulphuric acid or zinc chloride leads to products which are distinct from those obtained in the reaction of the olefins with per-acids (unpublished observations). It was, however, observed that both the glycols gave the corresponding acetates of unsaturated alcohols in smaller or greater amount when they were refluxed for several hours with an excess of acetic anhydride. As the diacetates, which are formed at the same time, lose the elements of acetic acid on heating, it is probable that the unsaturated esters are formed from the diacetates during the refluxing. This decomposition of the glycol diacetates may contribute to the formation of unsaturated alcohols in the reaction with peracetic acid, and particularly so if the unhydrolysed product is subjected to a lengthy fractionation before hydrolysis. That this, however, is a minor factor is shown by the nature of the unsaturated monoacetates obtained from 2 : 4 : 4-trimethylpentane-1 : 2-diol diacetate; 4 : 4-dimethyl-2-hydroxymethylpent-1-ene is only a minor constituent of the mixture, whereas from the peracetic acid reaction it is the main alcohol.

It was observed that the alkaline hydrolysis of the acetates of the 2 : 4 : 4-trimethylpenten-1-ol gave a high-boiling product as well as the expected alcohols. This high-boiling material appears to be polymerised unsaturated alcohol and is probably identical with the ill-defined high-boiling material isolated in the reaction of α -diisobutylene with per-acids. Work on this is proceeding.

The opportunity was taken to compare the alcohols formed by the action of selenium dioxide on α - and β -diisobutylene with those isolated from the reaction of these olefins with peracetic acid. 2 : 4 : 4-Trimethylpent-1-ene gives 4 : 4-dimethyl-2-hydroxymethylpent-1-ene identical with that obtained by the action of peracetic acid. 2 : 4 : 4-Trimethylpent-2-ene, however, gives an *alcohol* quite distinct from that (III) obtained from 2 : 3-epoxy-2 : 4 : 4-trimethylpentane or from 2 : 4 : 4-trimethylpent-2-ene by the action of per-acids.

If the reaction between 2 : 4 : 4-trimethylpent-2-ene and selenium dioxide depended on the initial saturation of the double bond by selenium dioxide, the only alcohol possible is 2 : 4 : 4-trimethylpent-1-en-3-ol. The observations recorded here establish quite unambiguously that the formation of unsaturated alcohols is due to some other reaction.

EXPERIMENTAL.

(1) *The Reaction of 2 : 3-Epoxy-2 : 4 : 4-trimethylpentane with Sulphuric Acid.*—(a) A trace of concentrated sulphuric acid on a thin glass rod was introduced into a solution of the epoxide (19.8 g., n_D^{20} 1.4093) in 20 g. of glacial acetic acid. A faint yellow coloration developed in the neighbourhood of the glass rod and disappeared on complete mixing. When reaction set in, the temperature rose to 60°. After 48 hours' keeping, the solution was diluted with water and neutralised with aqueous alkali. The neutral oil thus obtained was separated by distillation into three main fractions: (i) <100°/27 mm., 9.80 g.; (ii) 112—117°/22 mm., 6.7 g.; (iii) 125—130°/22 mm., 2.45 g.

Fraction (i) was resolved by distillation into 2 : 4 : 4-trimethylpent-1-en-3-ol, b. p. 153—154°, n_D^{20} 1.4376, *p*-nitrobenzoate, m. p. and mixed m. p. 77—78° (Found: C, 65.0; H, 7.0; N, 5.1. Calc.:

C, 64.95; H, 6.9; N, 5.1%), and 2 : 2 : 3 : 3-tetramethylbutanal, isolated as semicarbazone, m. p. and mixed m. p. 212° (Found : C, 58.5; H, 10.4; N, 22.8. $C_9H_{16}ON_3$ requires C, 58.3; H, 10.3; N, 22.7%).

Fractions (ii) and (iii) were hydrolysed by aqueous alkali and distilled, yielding 2 : 4 : 4-trimethylpentene-2 : 3-diol, m. p. and mixed m. p. 65–66°, and 2 : 2 : 5 : 5-tetramethyl-3 : 6-di-tert-butyl-1 : 4-dioxan (Found : C, 75.5; H, 12.5. $C_{16}H_{32}O_2$ requires C, 74.9; H, 12.6%). The dioxan was unchanged by reaction with acetic anhydride in pyridine and reacted with 2 : 4-nitrophenylhydrazine in warm aqueous alcoholic sulphuric acid to give a dinitrophenylhydrazone, small yellow needles from carbon tetrachloride, ethyl alcohol, or acetic acid, m. p. 142–143°, depressed to 130–135° by admixture with the 2 : 4-dinitrophenylhydrazone of 2 : 4 : 4-trimethylpentanal (Found : C, 54.6; H, 6.4; N, 18.1. $C_{14}H_{20}O_4N_4$ requires C, 54.45; H, 6.5; N, 18.2%).

(b) 2 : 3-Epoxy-2 : 4 : 4-trimethylpentane (3.4 g.) was added to a cold solution of 2 c.c. of concentrated sulphuric acid in 7 c.c. of water, and the mixture shaken. After one hour, the oil was taken up in ether and treated as described above. 2 : 2 : 3 : 3-Tetramethylbutanal was isolated as semicarbazone, m. p. 212° (yield 0.18 g.). 2 : 4 : 4-Trimethylpent-1-en-3-ol, b. p. 152–155°, $n_D^{17.5}$ 1.4392, was identified by its constants and its 3 : 5-dinitrobenzoate, m. p. and mixed m. p. 120–121°. 2 : 4 : 4-Trimethylpentane-2 : 3-diol (0.95 g.), m. p. and mixed m. p. 65–66°, was isolated together with a small amount of higher-boiling material not further examined.

(2) Reaction of 1 : 2-Epoxy-2 : 4 : 4-trimethylpentane with Sulphuric Acid.—The epoxide (9.35 g.) was added to a cold solution of 2 c.c. of concentrated sulphuric acid in 7 c.c. of water, and the mixture shaken. Reaction set in after a short induction period and the mixture got very hot. After 3 hours, the reaction mixture was neutralised, and the oil distilled. Between 140° and 151°, largely at 149–151°, a fraction was collected (2.4 g.) consisting chiefly of 2 : 4 : 4-trimethylpentanal, n_D^{20} 1.4180; semicarbazone, m. p. 118–120° undepressed by admixture with a genuine specimen.

An intermediate fraction, b. p. 155–200°, was essentially alcoholic, but nothing homogeneous could be isolated from it. A considerable bulk of the product (3.0 g.) distilled at 140–145°/35 mm., n_D^{24} 1.4400, and consisted of 2 : 5-dimethyl-3 : 6-dineopentyl-1 : 4-dioxan, b. p. 137°/31 mm., $n_D^{16.5}$ 1.4424 (Found : C, 75.1; H, 12.7. Calc. for $C_{16}H_{32}O_2$: C, 74.9; H, 12.6%). A small amount of 2 : 4 : 4-trimethylpentane-1 : 2-diol was also isolated.

When the reaction between the epoxide and diluted sulphuric acid was carried out so that the temperature did not rise above 30°, the yield of glycol was increased at the expense of the dioxan.

(3) Reaction of 2 : 4 : 4-Trimethylpent-1-ene with Selenium Dioxide.—Finely powdered and sieved selenium dioxide (20 g.) was added gradually to an efficiently stirred solution of 2 : 4 : 4-trimethylpent-1-ene (60 g.) in 80 c.c. of freshly distilled acetic anhydride. There was no immediate reaction and the mixture was warmed gently during the addition of the remainder of the dioxide. The reaction was completed by heating under reflux for 10 hours. An unsaturated acetate was isolated by steam distillation, b. p. 189–192° (corr.), n_D^{20} 1.4327 (Found : C, 70.7; H, 10.7. $C_{10}H_{18}O_2$ requires C, 70.5; H, 10.7%) (yield of crude acetate, b. p. 179–194°, 17 g.).

Alkaline hydrolysis gave the unsaturated alcohol, b. p. 170–174°, n_D^{20} 1.4292, consisting largely of 4 : 4-dimethyl-2-hydroxymethylpent-1-ene, identified by its *p*-nitrobenzoate, m. p. and mixed m. p. 44–45° (Found : C, 64.7; H, 7.1; N, 5.2. Calc. : C, 64.95; H, 6.9; N, 5.1%).

(4) Reaction of 2 : 4 : 4-Trimethylpent-2-ene with Selenium Dioxide.—The oxidation was carried out as described above, the same amounts of reactants being used. The yield of unsaturated acetate was of the same order, b. p. 190.5–191.5° (corr.), n_D^{20} 1.4344 (Found : C, 70.7; H, 10.8. $C_{10}H_{18}O_2$ requires C, 70.5; H, 10.7%). Alkaline hydrolysis gave 2 : 4 : 4-trimethylpent-2-en-1-ol, b. p. 177.5–178.5° (corr.), n_D^{20} 1.4459 (Found : C, 74.65, 74.5; H, 12.7, 12.7. $C_8H_{16}O$ requires C, 74.9; H, 12.6%), with some lower-boiling fractions, b. p. 172–177.5°, n_D^{20} 1.4448–1.4458. The *p*-nitrobenzoate had m. p. 55–56° (Found : C, 64.7; H, 6.8; N, 5.4. $C_{15}H_{18}O_4N$ requires C, 64.95; H, 6.9; N, 5.1%), and the 3 : 5-dinitrobenzoate, slender needles from alcohol, had m. p. 80° (Found : C, 56.1; H, 5.6. $C_{15}H_{18}O_6N_2$ requires C, 55.7; H, 5.9%).

(5) Acetylation of 2 : 4 : 4-Trimethylpentane-1 : 2-diol.—The glycol (25 g.) was heated under reflux for 24 hours with 125 g. of acetic anhydride. The excess of anhydride was removed by hydrolysis with water, giving 2.96 g. of an unsaturated acetate, b. p. 180–195°, and 25.65 g. of the diacetate of 2 : 4 : 4-trimethylpentane-1 : 2-diol, b. p. 130–134°/32 mm., n_D^{20} 1.4330 (Found : C, 63.2, 63.0; H, 10.0, 9.7; Ac, 39.6, 40.2. $C_{10}H_{22}O_4$ requires C, 62.6; H, 9.6; Ac, 37.4%). Repeated distillation of the diacetate at ordinary pressure gave acetic acid (2.5 g., b. p. 115–119°; anilide, m. p. 114–115°) and 14.25 g. of unsaturated acetates, with 2.3 g. of unchanged diacetate.

Alkaline hydrolysis of the unsaturated acetates gave a mixture of isomeric 2 : 4 : 4-trimethylpentenols, b. p. 173–178°, n_D^{20} 1.4370–1.4380, from which a small amount of 4 : 4-dimethyl-2-hydroxymethylpent-1-ene was isolated as 3 : 5-dinitrobenzoate, m. p. and mixed m. p. 73–74°. No other product could be isolated in a sufficiently pure state for precise characterisation. It is clear, however, that the remainder of the mixture contained a high proportion of 2 : 4 : 4-trimethylpent-2-en-1-ol since it was hydrogenated (PtO₂-alcohol) to 2 : 4 : 4-trimethylpentan-1-ol, b. p. 170–171°, n_D^{25} 1.4260; 3 : 5-dinitrobenzoate, m. p. and mixed m. p. 72–73° (Whitmore *et al.*, *J. Amer. Chem. Soc.*, 1941, **63**, 652, give n_D^{20} 1.4278–1.4285; 3 : 5-dinitrobenzoate, m. p. 72.5–73.5°).

(6) Acetylation of 2 : 4 : 4-Trimethylpentane-2 : 3-diol.—The glycol (5 g.), heated with acetic anhydride (25 g.) for 24 hours, gave after hydrolysis of the excess of anhydride 2 : 4 : 4-trimethylpentane-2 : 3-diol diacetate, b. p. 126–128°/32 mm., n_D^{20} 1.4318 (Found : C, 63.3; H, 9.9; Ac, 38.2. $C_{12}H_{22}O_4$ requires C, 62.6; H, 9.6; Ac, 37.4%. $C_{10}H_{20}O_3$ requires C, 63.8; H, 10.7; Ac, 22.9%), and 2.7 g. of the pure acetate of 2 : 4 : 4-trimethylpent-1-en-3-ol, b. p. 174–176°, n_D^{20} 1.4220 (Found : C, 70.65; H, 10.7. $C_{10}H_{18}O_2$ requires C, 70.5; H, 10.7%). Hydrolysis of the unsaturated acetate gave 2 : 4 : 4-trimethylpent-1-en-3-ol, b. p. 153°, n_D^{20} 1.4390; 3 : 5-dinitrobenzoate, m. p. and mixed m. p. 121°.