361. *The Reactions of Unsaturated Compounds. Part IX.* The Oxidation of* as-*Di*neo*pentylethylene by Chromic Oxide.*

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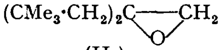
Oxidation of *as*-di*neo*pentylethylene by chromic oxide in acetic anhydride yields 1 : 2-epoxy-1 : 1-di*neo*pentylethane. The significance of this observation is discussed.

IT is shown below that oxidation of *as*-di*neo*pentylethylene (4 : 4-dimethyl-2-*neo*pentylpent-1-ene) (I) by chromium trioxide in acetic anhydride solution yields 1 : 2-epoxy-1 : 1-di*neo*pentylethane (II) as the main product; a small amount of di*neo*pentylacetic acid (III) is also formed. No other product could be isolated or identified.

Bartlett, Fraser, and Woodward's observations (*J. Amer. Chem. Soc.*, 1941, **63**, 496) that this epoxide is not hydrated to a glycol by dilute sulphuric acid have been confirmed and extended. It has not been possible to obtain the glycol from it even by prolonged boiling with aqueous alcohol; when it was sought to convert it into the chlorohydrin by the action of hydrogen chloride in ether (Swern *et al.*, *Ind. Eng. Chem. Anal.*, 1947, **19**, 414) there was no measurable uptake of hydrogen chloride; the epoxide did not react with sodiomalonic ester. Aqueous acids isomerise it to di*neo*pentylacetaldehyde, which is readily oxidised to di*neo*pentylacetic acid (III). This acid is also formed in good yield by oxidation of (I) or of (II) by chromic acid in aqueous sulphuric acid (Whitmore and Surmatis, *J. Amer. Chem. Soc.*, 1941, **63**, 2200; Bartlett, Fraser, and Woodward, *loc. cit.*).

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


$(CMe_3{\cdot}CH_2)_2\underset{\diagdown O \diagup}{C{-\!\!-}CH_2}$
(II.)

$(CMe_3{\cdot}CH_2)_2CH{\cdot}CO_2H$
(III.)

It was suggested by Byers and Hickinbottom (*J.*, 1948, **1334**) that the oxidation of an olefin by chromic acid in aqueous sulphuric acid depends on the initial formation of an epoxide, and that the course of the oxidation is determined by the behaviour of the epoxide in aqueous acid. The observations on the oxidation of di*neo*pentylethylene provide satisfactory support for this hypothesis, in that the almost quantitative isomerisation of the epoxide to di*neo*pentylacetaldehyde and its subsequent oxidation to di*neo*pentylacetic acid is in striking qualitative agreement with the formation of di*neo*pentylacetic acid as the main product of oxidation of the olefin.

If the isomerisation of the epoxide is accompanied by the formation of the glycol, it is postulated that the oxidation of the olefin by chromic acid in aqueous sulphuric will lead to a mixture of products derived from the oxidative fission of the glycol and from the oxidation of the isomerisation product. These deductions are borne out by the behaviour of 2 : 4 : 4-trimethylpent-1-ene (IV), which yields 2 : 4 : 4-trimethylpentanoic acid (V) † as well as methyl *neo*pentyl ketone (VI). The formation of 2 : 2 : 3 : 3-tetramethylbutanoic acid (VIII), acetone, and trimethylacetaldehyde from 2 : 4 : 4-trimethylpent-2-ene (VII) is a further example supported by observations on the corresponding epoxide (Byers and Hickinbottom, *loc. cit.*; Whitmore *et al.*, *J. Amer. Chem. Soc.*, 1941, **63**, 2028).

$CMe_3{\cdot}CH_2{\cdot}CMe{:}CH_2$
(IV.)

$CMe_3{\cdot}CH_2{\cdot}CHMe{\cdot}CO_2H$
(V.)

$CMe_3{\cdot}CH_2{\cdot}COMe$
(VI.)

$CMe_3{\cdot}CH{:}CMe_2$
(VII.)

$CMe_3{\cdot}CMe_2{\cdot}CO_2H$
(VIII.)

The formation of epoxides from olefins by the action of chromium trioxide has also been realised in acetic acid solution. Tetraphenylethylene and some of its halogen and nitro-derivatives (Behr, *Ber.*, 1872, **5**, 277; Norris, Thomas, and Brown, *Ber.*, 1910, **43**, 2954; Biltz, *Annalen*, 1897, **296**, 23; Bockemüller and Jansen, *ibid.*, 1939, **542**, 166), some 8 : 14- and 8 : 9-unsaturated sterols (Staveley and Bollenback, *J. Amer. Chem. Soc.*, 1943, **65**, 1285, 1290, 1600; Wintersteiner and Moore, *ibid.*, p. 1513), and some αβ-unsaturated steroid alcohols (Petrow *et al.*, *J.*, 1939, 998; 1940, 60) are reported to form epoxides when oxidised in acetic acid by chromic oxide. It seems a reasonable inference that the initial phase of the oxidation by chromium trioxide is the same whether it be in acetic acid or in acetic anhydride. The

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* Part VIII, *J.*, 1948, 1334.

† Geneva notation, $CO_2H = 1$, is used for these acids.

comparative stability of these epoxides no doubt permits of their survival during the reaction. Less stable oxides cannot survive in these conditions, yet it has been possible to obtain unambiguous evidence of their participation in some oxidations (Hickinbottom and Wood, unpublished; Fieser and Fieser, " Natural Products related to Phenanthrene," 1949, p. 231).

In the oxidation of olefins by chromic acid in aqueous sulphuric acid it is improbable if epoxides are formed that they can survive. Evidence of their participation in the reaction must rely on their isomerisation to aldehydes and ketones Experimental evidence of this nature has already been surveyed in the earlier part of this discussion.

It has sometimes been suggested that the oxidation of the olefinic double bond by chromic acid occurs through the initial formation of a glycol (compare Farmer and Pitkethly, *J.*, 1938, 287). Whatever may be the course of the reaction in special circumstances, it is unlikely that oxidation in general can occur in this way; it is known that the oxidative fission of 1 : 2-glycols by chromic acid occurs very easily (Byers and Hickinbottom, *loc. cit.*; cf. also Slack and Waters, *J.*, 1949, 594), and more rapidly than the glycol can isomerise in aqueous sulphuric acid to yield products which are characteristic of isomeric change in the oxidation.

EXPERIMENTAL.

(Analyses by Drs. Weiler and Strauss.)

Di*neo*pentylethylene(4 : 4-dimethyl-2-*neo*pentylpent-1-ene) was prepared from redistilled technical tri*iso*butylene by Bartlett, Fraser, and Woodward's method (*J. Amer. Chem. Soc.*, 1941, **63**, 495) with the modification that the amount of potassium permanganate was increased to 1200 g. for the oxidation of 168 g. of tri*iso*butylene. One sample of tri*iso*butylene with a low content of di*neo*pentylethylene required two such oxidations before a pure sample of the olefin was obtained.

Di*neo*pentylethylene prepared in this way from two different samples of tri*iso*butylene had b. p. 179°/760 mm., 112—113°/100 mm., 75°/32 mm. (all uncorr.); n_D^{20} 1·4283—1·4289. It was distilled over sodium before use.

1 : 2-Epoxy-1 : 1-di*neo*pentylethane(2 : 2′-di*neo*pentyloxiran) (II) was prepared from di*neo*pentylethylene by the action of perbenzoic acid in chloroform. Its constants, b. p. 90°/20 mm., n_D^{20} 1·4331, agree with those recorded by Bartlett, Fraser, and Woodward (*loc. cit.*), *viz.*, 85—88°/15 mm., n_D^{20} 1·4330.

The facile isomerisation of the epoxide to di*neo*pentylacetaldehyde (3 : 3-dimethyl-2-*neo*pentylbutanal) under the influence of dilute acids was confirmed. It readily yields *di*neo*pentylacetaldehyde 2 : 4-dinitrophenylhydrazone*, orange needles, m. p. 185° (Found : C, 59·7; H, 7·3; N, 15·1. $C_{18}H_{28}O_4N_4$ requires C, 59·3; H, 7·7; N, 15·4%) when mixed with an alcoholic solution of 2 : 4-dinitrophenylhydrazine containing some concentrated sulphuric acid.

In other respects the epoxide is relatively stable. It is substantially unchanged when refluxed with sodium for 10 minutes; it could not be induced to react with sodiomalonic ester. No glycol could be obtained by refluxing it with aqueous alcohol for 178 hours followed by keeping the product at room temperature for six weeks. The products from 3·1 g. of epoxide were di*neo*pentylacetic acid (1·0 g.) and a neutral fraction (1·1 g.), b. p. 94—110°/25 mm., which gradually solidified in the air with the formation of di*neo*pentylacetic acid; a residue (0·1 g.) could not be further identified. Attempts to estimate the epoxide by measuring the uptake of hydrogen chloride in ethereal solution gave no result.

Reduction of the epoxide in boiling ethereal solution by lithium aluminium hydride gave a mixture, b. p. 84—103°/18 mm., n_D^{20} 1·4359—1·4428, from which methyldi*neo*pentylcarbinol was isolated as its 3 : *5-dinitrobenzoate*, m. p. 138°, by chromatographing the esters of the crude alcohol (Found : C, 60·0; H, 7·25; N, 7·0. $C_{19}H_{28}O_6N_2$ requires C, 60·0; H, 7·4; N, 7·4%). The 3 : 5-dinitrobenzoate of 2 : 2-di*neo*pentylethanol was also isolated, m. p. and mixed m. p. 101°. The proportion of these two alcohols was not determined but it appears that methyldi*neo*pentylcarbinol is the more abundant.

For the purposes of comparison, 2 : 2-di*neo*pentylethanol was prepared by reduction of di*neo*pentylacetic acid by lithium aluminium hydride in boiling ether.

*Oxidation of Di*neo*pentylethylene by Chromium Trioxide in Acetic Anhydride.*—A number of these oxidations were carried out on the olefin which had been refluxed over sodium and redistilled immediately before use. The results in all oxidations were substantially the same. The following describes one such oxidation. A solution of chromium trioxide (14 g.) in freshly distilled acetic anhydride (80 ml.) was added during one hour to an efficiently stirred solution of di*neo*pentylethylene (n_D^{20} 1·4290; 40 g.) in acetic anhydride (38 ml.) cooled in ice–salt. When addition was complete, the solution was kept at below 0° and stirred continuously for 2 hours. Water (350 ml.) was then run in slowly, and the stirring and cooling continued till the hydrolysis of the anhydride was substantially complete. The upper layer was then separated and combined with two ether extracts of the aqueous layer. After being washed repeatedly with concentrated sodium carbonate solution and dried (K_2CO_3), it was distilled : fraction (*a*), b. p. 76—84°/34 mm., $n_D^{20\cdot1}$ 1·4285—1·4288, consisted essentially of unchanged olefin; the main product of the oxidation (*b*) was collected at 95—100°/27 mm. (11 g.); there was also a small residue of di*neo*pentylacetic acid ($\beta\beta$-dimethyl-α-*neo*pentylbutyric acid).

From (*b*) a substantially pure product was isolated by further fractionation; b. p. 95—96°/25 mm., n_D^{20} 1·4326—1·4329, d^{20} 0·8374. These constants agree well with those of 1 : 2-epoxy-1 : 1-di*neo*pentylethane (b. p. 90°/20 mm., 100°/32 mm.; n_D^{20} 1·4331; d^{20} 0·8367). A portion (2·2 g.) gave 2·0 g. unchanged after reaction with Girard T reagent. This material was unaltered after being heated with sodium

(0·2 g.) for 15 minutes; n_D^{20} 1·4340 [Found : C, 78·4; H, 13·0%; *M* (Rast), 179. Calc. : C, 78·2; H, 13·1%; *M*, 184]. The absence of any considerable amount of di*neo*pentylacetaldehyde was shown not only by its indifference to Girard reagent but also by its stability on exposure to air for several days. In contact with a little dilute sulphuric acid, it gradually solidifies to di*neo*pentylacetic acid; with an alcoholic sulphuric acid solution of 2 : 4-dinitrophenylhydrazine, the 2 : 4-dinitrophenylhydrazone of di*neo*pentylacetaldehyde was formed, m. p. and mixed m. p. 185°. Reduction in boiling ether by lithium aluminium hydride yielded methyldi*neo*pentylcarbinol, characterised by its 3 : 5-dinitrobenzoate, m. p. and mixed m. p. 138°.

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