266. *Reactions of Unsaturated Compounds. Part VIII. The Course of the Oxidation of Di*iso*butylene by Chromic Acid.*

By A. Byers and W. J. Hickinbottom.

Oxidation of 2 : 4 : 4-trimethylpent-1-ene by chromium trioxide in acetic anhydride gives a neutral product consisting largely of 1 : 2-epoxy-2 : 4 : 4-trimethylpentane; 2 : 2-dimethylpentan-4-one, 2 : 4 : 4-trimethylpentanal, and 2 : 4 : 4-trimethylpentane-1 : 2-diol are also formed. Technical di*iso*butylene behaves similarly to give a mixture of the epoxides derived from α- and β-di*iso*butylene. The epoxide is considered to be the first realisable product of this oxidation.

If it is assumed that the initial phase in the oxidation of di*iso*butylene by chromic acid in aqueous sulphuric acid is also the epoxide, it is possible to account satisfactorily for the formation of αγγ-trimethyl-*n*-valeric acid in this reaction. On this hypothesis ααββ-tetramethyl-*n*-butyric acid should be formed in small amount from β-di*iso*butylene. This acid has now been isolated from the products of the oxidation of technical di*iso*butylene.

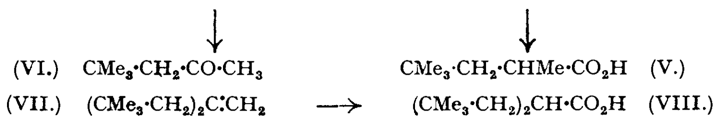
If the hypothesis is extended to other olefins a satisfactory explanation is provided for the so-called abnormal products of the oxidation of olefins.

The oxidation of the olefinic double bond by chromic acid in aqueous sulphuric acid generally leads to the fission of the double bond with formation of acids and ketones : $\mathrm{R{\cdot}CH{:}CR'R'' \longrightarrow R{\cdot}CO_2H + R'{\cdot}CO{\cdot}R''}$. A few olefins are reported to give abnormal products in that a smaller or greater proportion of an acid containing the same number of carbon atoms as the original olefin is formed. For instance, technical di*iso*butylene [a mixture of *ca.* 20% of 2 : 4 : 4-trimethylpent-2-ene and 80% of 2 : 4 : 4-trimethylpent-1-ene (I)] on oxidation with an aqueous sulphuric acid solution of chromic acid gives acetone, 2 : 2-dimethylpentan-4-one (VI), and trimethylacetic acid as major products with notable amounts of an octoic acid, $C_8H_{16}O_2$ (Butleroff, *Annalen*, 1877, **189**, 44; Homeyer, Whitmore, and Wallingford, *J. Amer. Chem. Soc.*, 1933, **55**, 4211). This acid has been identified as αγγ-trimethyl-*n*-valeric acid (V) by an unambiguous synthesis (Whitmore *et al.*, *ibid.*, 1941, **63**, 2028) and its formation must be considered as abnormal in that it contains the same number of carbon atoms as the original olefin. The oxidation of di*neo*pentylethylene (VII) to yield some di*neo*pentylacetic acid (VIII) is further example. The literature contains other less well authenticated records of the formation of an acid having the same number of carbon atoms as the original olefin, *viz.*, an octoic acid in small yield from oct-1-ene (Treibs and Schmidt, *Ber.*, 1928, **61**, 462), the oxidation of ethylene to give some acetaldehyde and acetic acid, and of propylene to yield acetone (Berthelot, *Annalen*, 1869, **150**, 373; Zeidler, *ibid.*, 1879, **197**, 246). Another manifestation of abnormality in this oxidation is the formation of an acid having a carbon skeleton differing from that of the original olefin. The oxidation of tetramethylethylene to yield some trimethylacetic acid is an example (Butleroff, *Ber.*, 1879, **12**, 1486).

Whitmore and Wilson (*J. Amer. Chem. Soc.*, 1934, **56**, 1397) have proposed a scheme for the abnormal course of the oxidation, depending on the addition of oxygen to the polarised double bond to form a carbonium ion which by a hydrogen shift gives an aldehyde. An alternative hypothesis would be to assume the formation of some isolable intermediate such as a glycol which can undergo rearrangement under the conditions of the oxidation. To test this latter view, the oxidation of di*iso*butylene in acetic anhydride by chromium trioxide was examined.

The oxidation of α-di*iso*butylene (2 : 4 : 4-trimethylpent-1-ene) gave a neutral product which contained a high proportion of 1 : 2-epoxy-2 : 4 : 4-trimethylpentane (II) with smaller amounts of 2 : 2-dimethylpentan-4-one (VI), 2 : 4 : 4-trimethylpentanal (III), and 2 : 4 : 4-trimethylpentane-1 : 2-diol (IV).

A similar result was obtained with technical di*iso*butylene : a mixture of the epoxides derived from α- and β-isomers with trimethylacetaldehyde (XIII), and 2 : 4 : 4-trimethylpent-1-en-3-ol in addition to the other products derived from α-di*iso*butylene.



$$\begin{array}{llcll}
\text{(I.)} & \mathrm{CMe_3{\cdot}CH_2{\cdot}CMe{:}CH_2} & \longrightarrow & \mathrm{CMe_3{\cdot}CH_2{\cdot}\underset{\diagdown O \diagup}{CMe{\cdot}CH_2}} & \text{(II.)} \\
 & & & \downarrow & \\
\text{(IV.)} & \mathrm{CMe_3{\cdot}CH_2{\cdot}C(OH)Me{\cdot}CH_2{\cdot}OH} & & \mathrm{CMe_3{\cdot}CH_2{\cdot}CHMe{\cdot}CHO} & \text{(III.)} \\
 & \downarrow & & \downarrow & \\
\text{(VI.)} & \mathrm{CMe_3{\cdot}CH_2{\cdot}CO{\cdot}CH_3} & & \mathrm{CMe_3{\cdot}CH_2{\cdot}CHMe{\cdot}CO_2H} & \text{(V.)} \\
\text{(VII.)} & \mathrm{(CMe_3{\cdot}CH_2)_2C{:}CH_2} & \longrightarrow & \mathrm{(CMe_3{\cdot}CH_2)_2CH{\cdot}CO_2H} & \text{(VIII.)}
\end{array}$$

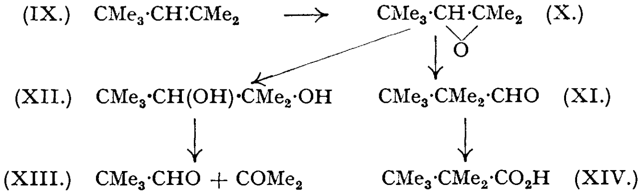
The formation of an epoxide in this reaction was unexpected, but there seems to be no reasonable doubt that it represents the simplest product of the oxidation that can be isolated.

A discussion of the significance of this result on the reduction of chromium trioxide is deferred till further work has been completed on this aspect. There is, however, sufficient experimental evidence to permit the course of the oxidation of an olefin to be followed through all its intermediate stages to the final products if the assumption is made that chromic acid behaves in the same way as chromium trioxide to give an epoxide as the initial product.

The behaviour of the epoxide in presence of aqueous sulphuric acid is a factor determining the course of the reaction. When the glycol is the sole product of the hydration of the epoxide, the resulting glycol undergoes fission by the oxidising agent to give normal products. If, however, the hydration is accompanied by isomerisation to carbonyl compounds or unsaturated alcohols then abnormal products may be formed.

The behaviour of the epoxides derived from α- and β-di*iso*butylene towards aqueous sulphuric acid has already been examined (this vol., p. 1331). When 1 : 2-epoxy-2 : 4 : 4-trimethylpentane (II) is treated with aqueous sulphuric acid of the same strength as that used in the oxidation, not only the corresponding glycol (IV) but notable amounts of 2 : 4 : 4-trimethylpentanal (III) and a cyclic diether are the principal products. These observations provide a satisfactory explanation of the formation of αγγ-trimethyl-*n*-valeric acid from α-di*iso*butylene by the action of chromic acid in aqueous sulphuric acid; 2 : 2-dimethylpentan-4-one is obtained by oxidative fission of the glycol.

2 : 3-Epoxy-2 : 4 : 4-trimethylpentane (X) yields the corresponding glycol (XII), 2 : 4 : 4-trimethylpent-1-en-3-ol and a small amount of 2 : 2 : 3 : 3-tetramethylbutanal (XI) by the action of aqueous sulphuric acid. The oxidative fission of the glycol gives acetone and trimethylacetaldehyde and thence trimethylacetic acid. 2 : 2 : 3 : 3-Tetramethylbutanal would give rise to the corresponding acid (XIV). This acid has not previously been identified as an oxidation product of β-di*iso*butylene.



A search was made in the acidic products of the oxidation of technical di*iso*butylene, and ααββ-tetramethyl-*n*-butyric acid was isolated by taking advantage of its low rate of esterification and its high melting point. This observation very strongly supports the hypothesis that the oxidation of di*iso*butylene by aqueous chromic acid in diluted sulphuric acid proceeds through the intermediate phase of the epoxide.

The hypothesis is still further supported by its application to the oxidation of those olefins which are known to give abnormal products (p. 1334). Of these, it is sufficient only to refer to the reported formation of trimethylacetic acid from tetramethylethylene. The epoxide of tetramethylethylene is known to give pinacolin as well as the corresponding glycol by the action of acid (Delacre, *Bull. Soc. chim.*, 1908, **3**, 211). The trimethylacetic acid arises from the pinacolin which is thus formed.

EXPERIMENTAL.

Oxidation of 2 : 4 : 4-*Trimethylpent*-1-*ene by Chromium Trioxide in Acetic Anhydride.*—A solution of chromium trioxide (50 g.) in 200 c.c. of freshly distilled acetic anhydride was added slowly and regularly during 2½ hours to 2 : 4 : 4-trimethylpent-1-ene (142 g.) (freshly distilled over sodium) diluted with 200 c.c. of acetic anhydride. Cooling by a bath of ice and salt is necessary as well as efficient stirring if the reaction is to proceed smoothly. After keeping overnight, the excess of acetic anhydride was hydrolysed by adding 1500 c.c. of ice-water, and the mixture was stirred and cooled till hydrolysis was complete. The oil which separated was removed, shaken repeatedly with aqueous sodium carbonate, and dried in contact with potassium carbonate. Distillation through an efficient column removed unchanged di*iso*butylene (95 g.; $n_D^{19^\circ}$ 1·4089) and left a liquid (A) which distilled largely at 130—155° (17·4 g.; $n_D^{20^\circ}$ 1·4132—1·4180) and a higher-boiling residue (B) (3·45 g.).

(a) *Identification of* 1 : 2-*epoxy*-2 : 4 : 4-*trimethylpentane.* Distillation of fraction (A) through a packed column gave a main fraction, b. p. 137—142° (10·6 g., $n_D^{19^\circ}$ 1·4145—1·4156) (Found : C, 74·8; H, 12·6. Calc. : C, 74·9; H, 12·0%), with small amounts of higher- and lower-boiling fractions. On heating all these fractions under reflux for 36 hours with aqueous alcohol and distilling the product, a lower-boiling fraction (C) (b. p. <100°/25 mm., 5·45 g.) was obtained, together with 2 : 4 : 4-trimethylpentane-1 : 2-diol (b. p. 108—120°/25 mm., 8·65 g.), m. p. 62—63° after crystallisation from light petroleum (b. p. 40—60°). There was no depression on admixture with a genuine specimen.

(b) *Identification of* 2 : 2-*dimethylpentan*-4-*one and of* 2 : 4 : 4-*trimethylpentanal.* The lower-boiling fractions (C) were separated by fractionation into (i) <120, (ii) 120—135°, (iii) 135—145°, (iv) 145—160°, (v) residue. Fraction (ii) (0·5 g.) consisted largely of 2 : 2-dimethylpentan-4-one (semicarbazone, m. p. and mixed m. p. 174—176°). Fraction (iv) (1·3 g.) gave a positive Schiff reaction and consisted largely of 2 : 4 : 4-trimethylpentanal (semicarbazone, m. p. 116—117°, not depressed by an authentic specimen). The intermediate fraction (iii) contained both substances, as shown by their isolation as semicarbazones. The residue (v) reacted with 3 : 5-dinitrobenzoyl chloride in pyridine, but no crystalline ester could be separated.

(c) *Identification of* 2 : 4 : 4-*trimethylpentane*-1 : 2-*diol.* The higher-boiling residue (B) was hydrolysed with aqueous-alcoholic potash and gave on distillation up to 100°/25 mm., 0·2 g.; 110—115/25 mm., 0·86 g. This last fraction solidified, and from it 2 : 4 : 4-trimethylpentane-1 : 2-diol was isolated by crystallisation from light petroleum (b. p. 40—60°); m. p. and mixed m. p. 62—63°.

*Oxidation of Technical Di*iso*butylene by Chromium Trioxide in Acetic Anhydride.*—Pure technical di*iso*butylene was purified by shaking with aqueous alkali to destroy peroxides and refluxing over sodium. The material used in this work boiled between 100° and 102°, $n_{\mathrm{D}}^{20^\circ}$ 1·4081—1·4092, and consisted of 2 : 4 : 4-trimethylpent-1-ene with a small amount of the isomeric 2 : 4 : 4-trimethylpent-2-ene.

The oxidation was carried out precisely as described in the previous section, 133 g. of di*iso*butylene and 50 g. of chromium trioxide being used. The neutral oil from the oxidation was separated by distillation into : (*a*) trimethylacetaldehyde (semicarbazone, m. p. and mixed m. p. 185—186°; yield of semicarbazone, 1·65 g.); (*b*) unchanged di*iso*butylene, 55 g.; (*c*) higher-boiling fractions.

The fraction (*c*) (total 24·2 g.) was separated by distillation into a number of fractions boiling between 105° and 160° (A) with a residue (B). The greater part of (A) was collected between 130° and 145° (13·15 g., $n_{\mathrm{D}}^{20^\circ}$ 1·4080—1·4139) and was a mixture which could not economically be separated into its constituents by distillation. Accordingly, it was heated under reflux with aqueous alcohol for 36 hours to convert the epoxides into the corresponding glycols. Distillation then gave : (*a*) <130°, 1·1 g.; (*b*) 130—145°, 1·7 g.; (*c*) 145—160°, 3·5 g.; (*d*) <90°/20 mm., 0·3 g.; (*e*) 95—102°/20 mm., 1·6 g.; (*f*) 102—115°/20 mm., 5·35 g.; (*g*) 115—120°/20 mm., 1·9 g. Fractions (*f*) and (*g*) deposited crystals of 2 : 4 : 4-trimethylpentane-1 : 2-diol on nucleation, m. p. 62—63 after crystallisation from light petroleum (b. p. 40—60°); there was no depression of m. p. on admixture with a genuine specimen. Fraction (*e*) gave a small amount of crystalline material on nucleation with 2 : 4 : 4-trimethylpentane-2 : 3-diol, m. p. and mixed m. p. 65° after crystallisation from light petroleum (b. p. 60—80°).

The presence of 2 : 2-dimethylpentan-4-one in fractions (*a*) and (*b*) was established by the preparation of its semicarbazone, m. p. and mixed m. p. 175—176°. An aldehyde was also present in fraction (*b*) as shown by a positive reaction with Schiff's reagent, but the amount was insufficient for exact identification. Fraction (*c*) was unsaturated and largely alcoholic. From it a 3 : 5-dinitrobenzoate was obtained, the m. p. of which was raised to 108—110° after repeated crystallisation and to 114—118° by admixture with a specimen of the 3 : 5-dinitrobenzoate of 2 : 4 : 4-trimethylpent-1-en-3-ol.

The residue (B) was obviously a mixture boiling over the range 50°/20 mm.—155°/20 mm. After alkaline hydrolysis followed by distillation it was separated into two main fractions : (*a*) b. p. 130—170° (3·6 g.), from which 2 : 4 : 4-trimethylpent-1-en-3-ol was isolated as 3 : 5-dinitrobenzoate, m. p. 118° raised to 120° by admixture with a genuine specimen; (*b*) b. p. 110—125/30 mm., which deposited crystals of 2 : 4 : 4-trimethylpentane-1 : 2-diol.

*Oxidation of Di*iso*butylene by Chromic Acid : Isolation of* ααββ-*Tetramethyl*-n-*butyric Acid.*—A solution of sodium dichromate (400 g.) in 700 c.c. of water and 220 c.c. of concentrated sulphuric acid was added gradually to 112 g. of redistilled technical di*iso*butylene (b. p. 101—102°; 20% trimethylpent-2-ene and 80% 2 : 4 : 4-trimethylpent-1-ene) in a 3-l. flask fitted with a reflux condenser, dropping funnel, and efficient stirrer. The olefin was warmed to 25° before adding the oxidising agent and the rate of addition was regulated so that the temperature did not rise above 40°. Efficient and vigorous stirring was necessary. The oxidation was completed by several days' keeping with occasional stirring. The volatile products were isolated by dilution and distillation in steam. The oil which passed over in the distillate was separated with the aid of potassium carbonate and consisted essentially of acetone and 2 : 2-dimethylpentan-4-one, with unchanged di*iso*butylene and small amounts of other products.

The aqueous portion of the distillate was concentrated after being made alkaline. The acids liberated from this solution were separated by fractional distillation into trimethylacetic acid (*p*-toluidide, m. p. 120—121°) and crude αγγ-trimethyl-*n*-valeric acid, b. p. 200—215°. A small amount of an acid having the properties of *tert.*-butylacetic acid was also obtained; b. p. 175—185° (*p*-toluidide, m. p. 133—134°, depressed by admixture with the *p*-toluidide of αγγ-trimethyl-*n*-valeric acid).

The crude αγγ-trimethyl-*n*-valeric acid was esterified (EtOH–H_2SO_4), giving the pure *ethyl* ester, b. p. 178·4—178·5°/745 mm. (corr.), $n_{\mathrm{D}}^{18\cdot5^\circ}$ 1·4128 (Found : C, 70·4; H, 11·7. $C_{10}H_{20}O_2$ requires C, 69·9; H, 11·7%).

The unesterified portion deposited crystals, and a further quantity of crystalline material was obtained by further partial esterification of the liquid. This crystalline acid separates from light petroleum (b. p. 40—60°) in stellate groups of small arrowhead-shaped crystals. It crystallises well from ethyl acetate; m. p. 194—195° (sealed tube) with a tendency to sublime below 100° (Found : C, 66·5; H, 11·0. $C_8H_{16}O_2$ requires C, 66·6; H, 11·2%). This acid is identical with that obtained by the aerial oxidation of 2 : 2 : 3 : 3-tetramethylbutanal and is consequently *ααββ-tetramethyl*-n-*butyric acid.* The amount isolated was about 2½% of the weight of crude ααγ-trimethyl-*n*-valeric acid.

Oxidation of 2 : 4 : 4-*Trimethylpentane*-1 : 2-*diol.*—A solution of chromium trioxide in acetic acid was gradually added to the glycol in acetic acid. The reaction mixture became warm. It was diluted and steam-distilled. 2 : 2-Dimethylpentan-4-one was obtained, b. p. 123—126° (semicarbazone, m. p. and mixed m. p. 176°).

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DEPARTMENT OF CHEMICAL ENGINEERING,
UNIVERSITY OF BIRMINGHAM.

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