Reactions of Unsaturated Compounds. Part XII. The Course of Oxidation of Olefins by Chromic Acid.*

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The results of oxidation of some olefins by chromic acid in aqueous sulphuric acid and by chromic oxide in acetic anhydride, are compared, and a hypothesis to account for them is developed.

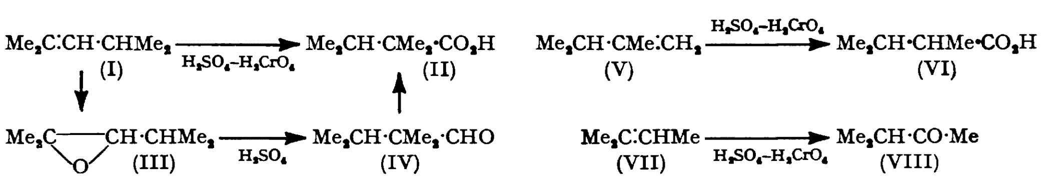
Two epoxides have been oxidised to 1 : 2-diketones.

Oxidation of 2 : 4-dimethylpent-2-ene (I) by chromic oxide in acetic anhydride diluted with carbon disulphide gives the corresponding epoxide (III) with no important quantity of other products. Other olefins examined in this work give lower yields and the products contain appreciable amounts of αβ-unsaturated ketones as well as substances derived from oxidative fission of the double bond. The products isolated from each olefin are given in the accompanying Table, the yield of epoxide descending in the order given.

It appears from these and earlier results (*J.*, 1948, **1334**; 1951, **1600**; 1953, **1906**; 1954, **4400**) that the yield of epoxide on oxidation by chromic oxide is greatest when one of the unsaturated carbon atoms of the olefin carries no hydrogen atom Thus *cyclo*hexene gave only a poor yield of epoxide and none could be isolated from pent-2-ene or oct-1-ene although the formation of an epoxide from oct-1-ene may be reasonably inferred from the formation of 1-acetoxyoctan-2-one when the oxidation is carried out in acetic acid. The low yield from these olefins may be due to competition with other reactions or to the instability of the epoxide in the oxidising solution. It is shown (p. 1364) that the αβ-diketones which are products of the oxidation of pent-2-ene and of *cyclo*hexene can arise by further oxidation of the epoxide.

Olefin	Products of oxidation
2 : 4-Dimethylpent-2-ene	Epoxide
2-Methylbut-2-ene	Epoxide, 3-methylbutan-2-one, 3-methylbut-2-enal, 3-methylbut-3-en-2-one
2 : 3-Dimethylbut-1-ene	Epoxide, 3-methylbutan-2-one, 2 : 3-dimethylbut-2-enal
*cyclo*Hexene	*cyclo*Hex-2-enone, epoxide, *cyclo*hexane-1 : 2-dione
Pent-2-ene	Pent-3-en-2-one, pentane-2 : 3-dione
Oct-1-ene	Hexanoic and heptanoic acid, oct-1-en-3-one (in acetic acid : 1-acetoxy-octan-2-one)

It was established earlier (*J.*, 1954, 4400) that oxidation of 2 : 3-dimethylbut-2-ene by chromic acid in aqueous sulphuric acid of more than 50% concentration gave appreciable amounts of 3 : 3-dimethylbutan-2-one. Under similar conditions, 2 : 4-dimethylpent-2-ene



(I) gives ααβ-trimethylbutyric acid (II) together with the normal products of oxidative fission, acetone and *iso*butyric acid. The acid (II) can be formed by oxidation of the rearrangement product in sulphuric acid of the glycol or of the epoxide (III).

The formation of 2 : 3-dimethylbutanoic acid (VI) from 2 : 3-dimethylbut-1-ene (V) and of 3-methylbutan-2-one (VIII) from 2-methylbut-2-ene (VII) can be accounted for similarly. Indeed all the recorded examples of the oxidation of an olefin by sulphuric–chromic acid to a product with the same number of carbon atoms (Butleroff, *Annalen*, 1877, **189**, 44; Whitmore and Surmatis, *J. Amer. Chem. Soc.*, 1941, **63**, 2200; Hickinbottom *et al.*, *locc. cit.*) find a simple explanation in terms of the intermediate formation

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of an epoxide or glycol. The assumption that a glycol is an intermediate is unlikely since no rearrangement products have been detected when glycols are treated with chromic acid in 55—60% sulphuric acid. Indeed oxidative fission of the glycol under these conditions is fast and vigorous.

If an epoxide is the intermediate in the sulphuric acid oxidation, it must take part in the reaction as the conjugate acid which may be formulated as $R_2\overset{+}{C}{\cdot}C(OH)R_2$. If so, the subsequent course of the reaction must be determined by the solvent. In aqueous solution containing a low concentration of acid, hydration to glycol is favoured and consequently its oxidative fission will account for the greater part of the products. With a relatively high concentration of sulphuric acid, hydration might reasonably be expected to give place to rearrangement by the generally accepted mechanism for the pinacol–pinacolone change.

It has not yet been possible to obtain direct evidence of the sequence of reactions leading to the formation of an epoxide or its conjugate acid from an olefin. The simple transfer of an oxygen atom from chromic oxide to the olefin satisfies the overall requirements of the oxidation, but it is more satisfactory to assume the initial formation of a complex between the olefin and chromic acid. The most convincing support for this view is found in the close resemblance between the oxidising action of chromyl chloride and that of chromic oxide on olefins and paraffins (Cristal and Eilar, *J. Amer. Chem. Soc.*, 1950, **72**, 4353; Hobbs and Houston, *ibid.*, 1954, **76**, 1254). The addition of chromyl chloride probably occurs by electrophilic attack at the double bond. The application of these ideas to chromic acid or chromic oxide oxidations leads to an initial compound which can be represented as $R_2\overset{+}{C}{\cdot}CR_2{\cdot}OCrO_2^-$. The epoxide can be derived from this in an anhydrous medium by the loss of $Cr^{IV}O_2$. In aqueous sulphuric acid the formation of the conjugate acid of an epoxide may be an unnecessary assumption if the complex can undergo hydration and oxidative fission or rearrange under the influence of sulphuric acid by the usually accepted pinacol–pinacolone change.

EXPERIMENTAL

2 : 4-Dimethylpent-2-ene (I).—2 : 4-Dimethylpent-2-ene, b. p. 83—84°, n_D^{20} 1·4018, was obtained by refluxing 2 : 4-dimethylpentan-3-ol with about four times its weight of oxalic acid (Wibaut *et al.*, *Rec. Trav. chim.*, 1943, **62**, 265, give b. p. 83·6°, n_D^{20} 1·4011). In several preparations a total of 185·6 g. was prepared from 346 g. of alcohol.

(a) *Oxidation by chromic oxide: formation of 2 : 3-epoxy-2 : 4-dimethylpentane.* 2 : 4-Dimethylpent-2-ene (66 g.) in carbon disulphide (100 ml.) was stirred in a 3-l. flask in ice–salt while chromic oxide (36 g.) in acetic anhydride (35 ml.) and carbon disulphide (300 ml.) was added dropwise during 2 hr. After a further 2 hr. a greenish-grey precipitate containing all the chromium was filtered off. The filtrate was shaken with saturated sodium carbonate solution and dried ($MgSO_4$; then K_2CO_3). After removal of the solvent and unchanged olefin, the main product was collected at 97—110° (14·2 g.) being essentially 2 : *3-epoxy-2 : 4-dimethylpentane*. A further fractionation gave the pure epoxide (9·7 g.), b. p. 110—110·5°, n_D^{20} 1·3961—1·3963 (Found : C, 73·4; H, 12·3. $C_7H_{14}O$ requires C, 73·6; H, 12·4%).

For comparison, 2 : 3-epoxy-2 : 4-dimethylpentane was prepared from the olefin by reaction with perbenzoic acid in ether; this had b. p. 110°, n_D^{20} 1·3956—1·3959. Both specimens had the same reactions and gave identical derivatives with the same m. p.s and no depression on admixture.

Reduction of the epoxide in ether by lithium aluminium hydride gives 2 : 4-dimethylpentan-2-ol, b. p. 130—132°, n_D^{20} 1·4140—1·4141, characterised by its 3 : 5-dinitrobenzoate, m. p. 70°. Huston and Smith (*J. Org. Chem.*, 1950, **15**, 1076) give m. p. 70°.

The epoxide reacts only very slowly with a solution of 2 : 4-dinitrophenylhydrazine in 2% aqueous hydrochloric acid. A copious yellow precipitate of *2 : 2 : 3-trimethylbutanal 2 : 4-dinitrophenylhydrazone*, m. p. 157—158°, was obtained immediately in warm 25% sulphuric acid (concentrations of sulphuric acid given in this paper are g. of acid in 100 g. of solution) (Found : C, 53·1; H, 6·3; N, 18·7. $C_{13}H_{18}O_4N_4$ requires C, 53·05; H, 6·2; N, 19·0%).

Shaking the epoxide with N-sulphuric acid gave 2 : 4-dimethylpentane-2 : 3-diol, m. p. 58—59°, not depressed on admixture with a specimen prepared from 2 : 4-dimethylpent-2-ene, in poor yield, by the action of *tert.*-butyl hydrogen peroxide and osmium tetroxide or, more conveniently, by the action of hydrogen peroxide in formic acid, followed by alkaline hydrolysis. The structure of the glycol was confirmed by fission by periodic acid to acetone and *iso*butaldehyde which were separated and identified as 2 : 4-dinitrophenylhydrazones. The separation was effected by chromatography on silica with benzene–light petroleum, and this method was used for all the mixtures of aldehydes and ketones described below.

The glycol rearranges in warm 40% aqueous sulphuric acid containing 2 : 4-dinitrophenylhydrazine to give the 2 : 2 : 3-trimethylbutanal 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 159° (see above).

(b) *Oxidation by chromic acid in aqueous sulphuric acid: formation of* 2 : 2 : 3-*trimethylbutanoic acid.* 2 : 4-Dimethylpent-2-ene (25 g.) was stirred with 66% sulphuric acid (150 ml.), cooled in ice, while chromic oxide (65 g.) in water (50 ml.) was added dropwise. Oxidation became progressively slower and it was necessary to stir for 2 hr. after the addition was complete. Then carboxylic acids were removed by ether-extraction, separated from neutral material (1·2 g.) by alkali, and fractionally distilled to give *iso*butyric acid, b. p. 63—70°/22 mm. (2·3 g.) (*p*-toluidide, m. p. and mixed m. p. 108°), and ααβ-trimethylbutyric acid (4·7 g.), b. p. 96—97°/16 mm. (Found: C, 64·9; H, 10·4. Calc. for $C_7H_{14}O_2$: C, 64·6; H, 10·8%). The latter acid is reported to melt at 50° (Haller and Bauer, *Compt. rend*, 1909, **149**, 6; Richard, *Ann. Chim. Phys.*, 1910, **21**, 353) but our specimen did not solidify. Its amide, m. p. 130°, was identical with ααβ-trimethylbutyramide prepared as described by Haller and Bauer (Found: C, 64·9; H, 11·7; N, 10·8. Calc. for $C_7H_{15}ON$: C, 65·1; H, 11·7; N, 10·8%); the *p-toluidide* had m. p. 92° (Found: C, 77·0; H, 10·0; N, 6·3. $C_{14}H_{21}ON$ requires C, 76·7; H, 9·7; N, 6·4%).

ααβ-Trimethylbutyric acid with lithium aluminium hydride in ether gave 2 : 2 : 3-trimethylbutan-1-ol, b. p. 55—60°/15 mm., n_D^{20} 1·4346, oxidised by *tert.*-butyl chromate to 2 : 2 : 3-trimethylbutanal (2 : 4-dinitrophenylhydrazone, m. p. 158—159° not depressed by a specimen obtained by rearrangement of 2 : 4-dimethylpentane-2 : 3-diol).

2-*Methylbut*-2-*ene* (VII).—2-Methylbut-2-ene, b. p. 38·6°, n_D^{20} 1·3870—1·3875, was prepared by slowly distilling 2-methylbutan-2-ol with 0·3% of its weight of iodine, and subsequently fractionating the mixture of olefins (438 g. from 784 g. alcohol, b. p. 31—39°) (yield, 114 g.).

Oxidation of the olefin in chloroform by perbenzoic acid gives 2 : 3-epoxy-2-methylbutane, b. p. 74—75°, which is reduced by lithium aluminium hydride to *tert.*-pentyl alcohol, b. p. 101—102°; a solution of 2 : 4-dinitrophenylhydrazine in 20% sulphuric acid gives an immediate precipitate of 2 : 4-dinitrophenylhydrazones of trimethylacetaldehyde, m. p. and mixed m. p. 208° in small yield, and of 3-methylbutan-2-one, m. p. and mixed m. p. 125°. The epoxide is hydrated by cold 5% hydrochloric acid to 2-methylbutane-2 : 3-diol, b. p. 75—76°/14 mm. The glycol was also prepared from ethyl lactate and methylmagnesium bromide and the two specimens had the same reactions: oxidative fission (periodic acid) gave acetaldehyde and acetone (separated and identified as 2 : 4-dinitrophenylhydrazones); rearrangement by warm 40% sulphuric acid containing 2 : 4-dinitrophenylhydrazine gave 3-methylbutan-2-one as the main product with some trimethylacetaldehyde, both isolated as 2 : 4-dinitrophenylhydrazones.

(i) *Oxidation by chromic oxide: formation of* 2 : 3-*epoxy*-2-*methylbutane and other products.* 2-Methylbut-2-ene (60 g.) in carbon disulphide (100 ml.) was oxidised by chromic oxide (50 g.) in acetic anhydride (50 ml.) and carbon disulphide under the conditions described on p. 1361. After removal of the solvent and unchanged olefin, 2 : 3-*epoxy*-2-*methylbutane*, b. p. 72—74°, n_D^{20} 1·3880—1·3887 (1·3 g.), was collected together with high-boiling material (A). In another oxidation, from 64 g. of olefin, 2·6 g. of epoxide were obtained (Found: C, 69·3; H, 11·9. $C_5H_{10}O$ requires C, 69·7; H, 11·7%). The identity was established by comparison with the epoxide and its derivatives prepared by the action of perbenzoic acid.

The material (A) was treated with water to remove acetic anhydride and on distillation gave 2-methylbutane-2 : 3-diol and a mixture of carbonyl compounds (1·6 g.), b. p. 30—56°/19 mm., n_D^{20} 1·4170—1·4196, which was resolved by chromatography of the 2 : 4-dinitrophenylhydrazones in silica (eluant benzene–light petroleum) into trimethylacetaldehyde in small amount, 3-methylbut-3-en-2-one, 3-methylbutan-2-one, and 3-methylbut-2-enal. These were identified by comparison with authentic specimens and the order given is that of their elution from silica. 3-Methylbut-3-en-2-one, b. p. 97°, n_D^{20} 1·4240, prepared by slowly distilling 3-hydroxy-3-methylbutan-2-one with toluene-*p*-sulphonic acid was characterised as 2 : 4-*dinitrophenylhydrazone*, orange needles (from ethyl acetate), m. p. 189—190° (Found: C, 49·8; H, 4·3; N, 21·5. $C_{11}H_{12}O_4N_4$ requires C, 50·0; H, 4·6; N, 21·3%). 3-Methylbut-2-enal, b. p. 126—130°, n_D^{20} 1·4543 (Fischer *et al.*, *Ber.*, 1931, **65**, 30, record b. p. 132—133°, n_D^{20} 1·4526), from the oxidation of 3-methylbut-2-en-1-ol with *tert.*-butyl chromate gave a 2 : 4-*dinitrophenylhydrazone*, m. p.

181·5° (Found: C, 50·2; H, 4·8%). The aldehyde is oxidised by chromic acid in dilute sulphuric acid to β-methylcrotonic acid, m. p. and mixed m. p. 70°.

(ii) *Oxidation by chromic acid in aqueous sulphuric acid: formation of* 3-*methylbutan*-2-*one.* The olefin (12·5 g.) was stirred with 55% sulphuric acid (45 ml.) at 0° while chromic oxide (28·5 g.) in 55% sulphuric acid (200 ml.) was added dropwise. The neutral product was 3-methylbutan-2-one (1·4 g.), b. p. 94—97° (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 126°).

2 : 3-*Dimethylbut*-1-*ene* (V).—This olefin, b. p. 55·6—55·8°, n_D^{20} 1·3899, was obtained as the lower-boiling constituent of the product of the dehydration of 2 : 3-dimethylbutan-2-ol (*J.*, 1954, 4200). It was distilled over sodium immediately before use.

(a) *Oxidation by chromic oxide: formation of* 1 : 2-*epoxy*-2 : 3-*dimethylbutane and* 3-*methylbutan*-2-*one.* (i) 2 : 3-Dimethylbut-1-ene (44 g.) was oxidised by chromic oxide (50 g.) in acetic anhydride (300 ml.) and the volatile products were distilled out of the mixture at 15 mm. into cold traps (solid carbon dioxide–acetone) until acetic anhydride began to distil. The distillate was diluted with ether and washed with water and aqueous potassium carbonate (acetone was present in the aqueous washings). Distillation through a column gave the following fractions after removal of solvent and unchanged olefin: (*a*) b. p. 56—80°, n_D^{20} 1·3890—1·3926, 0·6 g.; (*b*) b. p. 82—96°, n_D^{20} 1·3930—1·3967, 4·3 g.; (*c*) residue 0·4 g. The greater part of fraction (*b*) distilled at 94—97°, had n_D^{20} 1·3952—1·3960, and consisted of 1 : 2-epoxy-2 : 3-dimethylbutane, b. p. 95—96°, n_D^{20} 1·4020, and 3-methylbutan-2-one, b. p. 94°, n_D^{20} 1·3887. This was established by the following reactions: (*a*) A portion shaken for 2 days with 0·3N-hydrochloric acid gave 3-methylbutan-2-one, b. p. 90—100° (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 124°), and 2 : 3-dimethylbutane-1 : 2-diol, b. p. 90—93°/15 mm.; the glycol was rearranged by aqueous sulphuric acid to 2 : 3-dimethylbutanal (2 : 4-dinitrophenylhydrazone m. p. and mixed m. p. 125°), and on oxidation gave 3-methylbutan-2-one. (*b*) A warm solution of 2 : 4-dinitrophenylhydrazine in 25% sulphuric acid gave an immediate yellow precipitate from which 2 : 3-dimethylbutanal 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 125°, was readily isolated. (*c*) Reduction by lithium aluminium hydride in boiling ether and reaction of the alcohols thus formed with 3 : 5-dinitrobenzoyl chloride in pyridine gave two esters separated by chromatography on alumina; the less strongly adsorbed was identical with the 3 : 5-dinitrobenzoate, m. p. and mixed m. p. 107—108°, of 2 : 3-dimethylbutan-2-ol; the more strongly adsorbed was the ester, m. p. and mixed m. p. 78°, of 3-methylbutan-2-ol.

(ii) 2 : 3-Dimethylbut-1-ene (51 g.) was oxidised by chromic oxide (45 g.) in acetic anhydride (350 ml.) with the difference that water was added to hydrolyse the acetic anhydride and to convert any epoxide into glycol. The neutral product was separated into the following fractions: (*a*) b. p. 89—100°, n_D^{20} 1·390—1·3963, 0·9 g.; (*b*) b. p. 110—118°, n_D^{20} 1·4030—1·4170, 0·5 g.; (*c*) b. p. 40—60°/25 mm., n_D^{20} 1·4190—1·4198, 0·7 g.; (*d*) b. p. 70—73°/25 mm., n_D^{20} 1·4205—1·4207, 1·2 g.; (*e*) b. p. 94°/10 mm., n_D^{20} 1·4320—1·4360, 4·9 g. Fraction (*e*) is essentially 2 : 3-dimethybutane-1 : 2-diol and was identified by the reactions enumerated earlier. 2 : 3-Dimethylbutanal and 3-methylbutan-2-one were recognised as present in fractions (*a*) and (*b*), by isolation of dinitrophenylhydrazones and by reduction to the corresponding alcohols. From fractions (*c*) and (*d*) the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 195°, of 2 : 3-dimethylbut-2-enal was readily obtained.

(b) *Oxidation by chromic acid in aqueous sulphuric acid: formation of* αβ-*dimethylbutyric acid.* 2 : 3-Dimethylbut-1-ene (10·7 g.) and 50% sulphuric acid (100 ml.) were stirred and cooled in ice while chromic oxide (20 g.) in 50% sulphuric acid (300 ml.) was added dropwise. The neutral product boiled at 92—100° and consisted essentially of 3-methylbutan-2-one (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 125°). The acid product was αβ-dimethylbutyric acid, b. p. 95—96°/18 mm., n_D^{20} 1·4141—1·4146 (1·2 g.) (amide, m. p. and mixed m. p. 130°; *p*-phenylphenacyl ester, m. p. and mixed m. p. 74°).

2 : 3-Dimethylbutane-1 : 2-diol (5·5 g.) in 50 ml. of 50% aqueous sulphuric acid, oxidised by chromic acid in 50% sulphuric acid, gave 3-methylbutan-2-one. There was no evidence of the formation of αβ-dimethylbutyric acid or of any other product.

Oct-1-*ene*.—This olefin was a gift from the Anglo-Iranian Oil Co. Ltd. It was refluxed over sodium and fractionated before each oxidation (b. p. 122°, n_D^{20} 1·4095).

(i) *Oxidation by chromic oxide.* (a) In acetic acid: formation of 1-acetoxyoctan-2-one. A solution of oct-1-ene (121 g.) in acetic acid (200 ml.) was oxidised at 0° by the gradual addition of chromic oxide (55 g.) in acetic acid (500 ml.). From the neutral products 1-acetoxyoctan-2-one, m. p. and mixed m. p. 43°, was isolated from the fraction of b. p. 79—83°/13 mm. (2·8 g.)

and was further identified as its semicarbazone, m. p. and mixed m. p. 40°, and 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 159° (*J.*, 1954, 4200).

From the lower-boiling fraction, b. p. 70—110°/15 mm., oct-1-en-3-one was isolated as 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 124°, after chromatography on silica. Other carbonyl compounds were present in smaller amounts but none was isolated pure. The acidic products were not examined.

(b) In carbon disulphide and acetic anhydride. A cold solution of oct-1-ene (68·5 g.) in carbon disulphide (100 ml.) was oxidised by the gradual addition of chromic oxide (40 g.) in acetic anhydride (40 ml.) and carbon disulphide (200 ml.). Distillation of the neutral product gave a fraction, b. p. 58—74°/15 mm., n_D^{20} 1·4195—1·4260 (2·4 g.), from which oct-1-en-3-one was isolated as its 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 124°. The acid products (4·0 g.) distilled at 98—110°/13 mm., and had n_D^{20} 1·4180—1·4220. By fractional distillation, and crystallisation and chromatography of the *p*-toluidides, *N-p*-tolyl-hexanamide, m. p. 72°, and -heptanamide, m. p. 75°, were separated.

cyclo*Hexene.—Oxidation by chromic oxide: formation of* 1 : 2-*epoxy*cyclo*hexane*. *cyclo*Hexene (256 g.; b. p. 83°, n_D^{20} 1·4471) in carbon disulphide (300 ml.) was oxidised by chromic oxide (60 g.) in acetic anhydride (60 ml.) and carbon disulphide (200 ml.) under the conditions already described. The product was separated by distillation into unchanged olefin (230 g.), 1 : 2-epoxy*cyclo*hexane, b. p. 130—132°, n_D^{20} 1·4578 (1·3 g.), a fraction, b. p. 86—93°/50 mm., n_D^{20} 1·4844 (2·9 g.), consisting largely of *cyclo*hex-2-enone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 167°), and a residue (A) (0·6 g.). 1 : 2-Epoxy*cyclo*hexane was identified by conversion into *trans*-*cyclo*hexane-1 : 2-diol, m. p. and mixed m. p. 103—104°, and by reduction by lithium aluminium hydride to *cyclo*hexanol (3 : 5-dinitrobenzoate, m. p. and mixed m. p. 113°). The residue (A) contained *cyclo*hexane-1 : 2-dione [2 : 4-dinitrophenylhydrazone, scarlet needles (from ethyl acetate), m. p. and mixed m. p. 228°] and a small amount of *cyclo*hex-2-enone, which were isolated and separated as 2 : 4-dinitrophenylhydrazones. Chromatography of a portion of (A) on alumina gave a small amount of white solid, m. p. 120°, which contains 58% of hydrolysable acetate group.

Oxidation of 1 : 2-*Epoxy*cyclo*hexane*.—A solution of the epoxide (1·0 g.) in light petroleum was oxidised by *tert.*-butyl chromate (from 0·5 g. of chromic oxide) in light petroleum. A brown precipitate was formed slowly and after 3 hr. at room temperature, aqueous solutions of acetic and oxalic acids were added till the precipitate dissolved. From the ether extract *cyclo*hexane-1 : 2-dione was isolated as its red bis-2 : 4-dinitrophenylhydrazone, m. p. 228°.

*cyclo*Hexane-1 : 2-diol under similar conditions also gave *cyclo*hexane-1 : 2-dione.

For comparison, *cyclo*hexane-1 : 2-dione was prepared by refluxing *cyclo*hexanone with selenium dioxide for 3 hr. It boiled at 101—102°/25 mm. and gave a bis-2 : 4-dinitrophenylhydrazone, red crystals (from acetone), m. p. 230—232°, identical in every respect with that from 1 : 2-epoxy*cyclo*hexane and from *cyclo*hexane-1 : 2-diol. Campbell and McCall (*J.*, 1950, 2870) describe the bis-2 : 4-dinitrophenylhydrazone, m. p. 233—234° (Found : C, 45·7; H, 3·3; N, 23·9. Calc. for $C_{18}H_{16}O_8N_8$: C, 45·7; H, 3·4; N, 23·7%).

Pent-2-ene.—The olefin was a commercial sample, refluxed over sodium and fractionated to give material of constant b. p. 36° and n_D^{20} 1·3800.

(a) *Oxidation by chromic oxide.* A solution of the olefin (64 g.) in carbon disulphide (100 ml.) was oxidised under the conditions described above by chromic oxide (40 g.) in acetic anhydride (40 ml.) and carbon disulphide (300 ml.). The main bulk of the neutral product (4·3 g.) boiled at 100—120° and consisted essentially of pent-3-en-2-one with a small amount of pentane-2 : 3-dione, separated as, and recognised by crystallisation of, their 2 : 4-dinitrophenylhydrazones (see below). A small amount (0·9 g.) of neutral material, b. p. 70—85°, was also obtained which may have contained 2 : 3-epoxypentane (b. p. 84°), but no evidence of its presence could be obtained.

(b) *Oxidation of* 2 : 3-*epoxypentane.* The epoxide (1·5 g.) in light petroleum (b. p. $< 40°$) was oxidised by the addition of *tert.*-butyl chromate (from 0·5 g. of chromic oxide) in light petroleum. The neutral product was treated directly with 2 : 4-dinitrophenylhydrazine in alcoholic sulphuric acid, to give pentane-2 : 3-dione bis-2 : 4-dinitrophenylhydrazone, bronze red needles (from acetone), m. p. 274° (Found : C, 44·2; H, 3·5; N, 24·8. Calc. for $C_{17}H_{16}O_8N_8$: C, 44·4; H, 3·5; N, 24·4%). Heilbron, Jones, Smith, and Weedon (*J.*, 1946, 57) give m. p. 280—281°.

Oxidation of 2 : 3-epoxypentane or pentane-2 : 3-diol by chromic oxide in carbon disulphide and acetic anhydride also gave pentane-2 : 3-dione.

For comparison and identification, pentane-2 : 3-dione was prepared by refluxing pentan-2-one (24 g.) with selenium dioxide (10 g.) for 2 hr. A mixture, b. p. 100—110° (21·5 g.), of diketone and unchanged ketone was obtained. It was sufficient for the present work to convert the mixture into 2 : 4-dinitrophenylhydrazones which were separated by taking advantage of the sparing solubility of the derivative of the dione in benzene : this is best purified by extraction with acetone (Soxhlet) and has m. p. 274°.

Preparation of Pent-3-en-2-one.—Pent-3-en-2-ol, b. p. 122°, n_D^{20} 1·4276, was oxidised by *tert.*-butyl chromate in light petroleum to give pent-3-en-2-one, b. p. 120—122°, n_D^{20} 1·1441; Alexander and Coraor (*J. Amer. Chem. Soc.*, 1951, **73**, 2721) give b. p. 121—122°, n_D^{20} 1·4377. The 2 : 4-dinitrophenylhydrazone formed deep red crystals, m. p. 157; Jones and Whiting (*J.*, 1949, 1428) give m. p. 158—159°.

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