Oxidation Products of Diïsobutylene. Part I. Liquid-phase Oxidation of Diïsobutylene : Formation, Properties, and Analysis of 1 : 2-*Epoxy*-2 : 4 : 4-*trimethylpentane.*

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By oxidising 2 : 4 : 4-trimethylpent-1-ene (α-di*iso*butylene) with air under pressure at 130—140°, up to 56% yields of the derived epoxide (1 : 2-epoxy-2 : 4 : 4-trimethylpentane) are obtained, provided that the reaction medium is kept neutral or slightly alkaline. In the absence of any added base, the epoxide formed in the early stages of the oxidation later disappears, the final products being formic acid, 4 : 4-dimethylpentan-2-one, 2 : 4 : 4-trimethylpentane-1 : 2-diol, etc. These are also obtained as by-products in making the epoxide by the process just outlined. 2 : 4 : 4-Trimethylpent-2-ene (β-di*iso*butylene) also gives the corresponding epoxide under analogous conditions.

Difficulties have been experienced in applying functional-group analysis to these epoxides, and a new method is proposed.

A number of papers and patents have described the liquid-phase oxidation of olefins by molecular oxygen; a large variety of products has usually been reported, the most usual being carboxylic acids, alcohols, aldehydes, and ketones. There is little doubt that these are end-products of a series of reactions, and some investigators have attempted to arrest the oxidation at an earlier stage.

The autoxidation of commercial di*iso*butylene, a mixture of 2 : 4 : 4-trimethylpent-1-ene (80%) and -2-ene (20%), is mentioned specifically in only four publications. French Pat. 816,055/1937 claims the oxidation in the liquid phase of tertiary olefins with gaseous oxygen or peroxides in the presence of metallic catalysts. The products are stated to be mainly unsaturated alcohols and ketones. Bost (*Science*, 1938, **88**, 440) states that the oxidation of di*iso*butylene by molecular oxygen under pressure at elevated temperatures gave peroxides, aldehydes, ketones, and acids. Di*iso*butylene was also oxidised with oxygen at 100° and 100 lb./sq. in. pressure in the presence of solid potassium hydroxide (Bost and Lockhart, *J. Amer. Chem. Soc.*, 1941, **63**, 2790); qualitative tests on the product showed the presence of methyl ketones, acids, alcohols, and 1 : 2-glycols, and traces of peroxides and aldehydes. The substances specifically identified were acetone, 4 : 4-dimethylpentan-2-one, carbon dioxide, and formic and pivalic acids. In U.S.P. 2,475,605/1949 there is an example showing the oxidation of di*iso*butylene with air at 200 lb./sq. in. at 130—133° : the products are described as the lower oxidation products (alcohols, ethers, ketones, and aldehydes).

The formation of epoxides from autoxidation of olefins has been described by Paquot (Thesis, Paris, 1943) and by Schneider and Sommer (U.S.P. 2,052,195/1936.) This patent describes how, if oxygenation is carried out in presence of mild alkalis, the epoxide is protected against hydrolytic attack and remains in the product. A series of papers by Byers and Hickinbottom (*J.*, 1948, 284, 1328, 1331, 1334) upon the oxidation of di*iso*butylene with chemical reagents describes a number of the compounds that we have encountered.

In the present work, experiments were commenced in glass apparatus with oxygen at atmospheric pressure at 90—95°. Pure freshly distilled 2 : 4 : 4-trimethylpent-1-ene underwent oxidation thus in a typically autocatalytic manner; the oxygen absorption followed a sigmoid curve against time, as shown in Fig. 1*a*, which also shows the concentration of various products (measured by titration) during the experiment. As can be seen, peroxides remained almost constant, at about 2·5—3·5 mol. %, but acids, esters, and carbonyl compounds increased continuously. Considerable quantities of epoxide were detected in the earlier stages, increasing to a maximum of 8 mol. % but thereafter falling to zero. As will be shown later, the amounts of epoxide actually present would be somewhat higher than those found by titration. In presence of 0·1% of cobalt naphthenate, the concentration of peroxide was much lower throughout, and the oxidation showed no induction period (Fig. 1*b*).

The major components of the final product were formic acid, formates, 4 : 4-dimethylpentan-2-one, 2 : 4 : 4-trimethylpentane-1 : 2-diol, and a high-boiling oil typical of the dimeric condensation products obtained from 1 : 2-epoxy-2 : 4 : 4-trimethylpentane and its derivatives (cf. Part III, *J.*, 1954, 2180). A very similar mixture was obtained from atmospheric oxidation of 2 : 4 : 4-trimethylpent-1-ene (with 10% of the -2-ene) in a stainless-steel pressure vessel at 120° and 200 lb./sq. in. Little hydrocarbon remained; extended fractionation of the product gave 4 : 4-dimethylpentan-2-one (20% of theory), 2 : 4 : 4-trimethylpentane-1 : 2-diol and its formate (5% together), and the other compounds just mentioned.

In view of the potential value of the epoxide, attempts were then made to arrest the course of oxidation at that stage. Oxygenation in presence of bases to neutralise acids as they were formed, so stabilising the epoxide, led to about 50% yields of 1 : 2-epoxy-2 : 4 : 4-trimethyl pentane from commercial di*iso*butylene. Aqueous sodium carbonate was a suitable base, although magnesium oxide or a phosphate buffer could also be used. The oxidation was carried out batchwise by passing air at 200 lb./sq. in. (gauge) into di*iso*butylene at 140° with vigorous stirring, whilst aqueous sodium carbonate was pumped in at such a rate as to maintain the pH of the aqueous layer at 8—8·5. In an adaptation for continuous working, about the same yield of epoxide was obtained.

Small amounts of various metallic compounds, *e.g.*, cobalt, lead, manganese, or iron naphthenates, or sodium vanadate or tungstate, were normally added as initiators. When no initiator was added, the oxidation still appeared to proceed normally, with the yield of epoxide possibly slightly lowered. It is probable, however, that traces of metallic catalysts were always present in the system. There were no notable differences in yield with the various catalysts used, although alkali-soluble catalysts (vanadate and tungstate) gave a cleaner product.

The product was worked up by fractional distillation of the organic phase. Besides 1 : 2-epoxy-2 : 4 : 4-trimethylpentane (40—55% of theory on 2 : 4 : 4-trimethylpent-1-ene consumed) and unchanged hydrocarbon, there were obtained 4 : 4-dimethylpentan-2-one (10% on total di*iso*butylene consumed) and 2 : 3-epoxy-2 : 4 : 4-trimethylpentane (37% on 2 : 4 : 4-trimethylpent-2-ene), mainly together as an azeotrope; also, lower-molecular compounds such as acetone, methacraldehyde, and *tert.*-butanol, and higher-boiling products in which 2 : 4 : 4-trimethylpent-1-en-3-ol, 2-*neo*pentylprop-2-en-1-ol (see Part II, following paper), and 2 : 4 : 4-trimethylpentane-1 : 2-diol were recognised. The aqueous phase contained carboxylic acids, mainly ββ-dimethylbutyric and possibly pivalic and αγγ-trimethylvaleric. A weight balance on one batch experiment, oxidised to 48% conversion of hydrocarbon, was as follows:

Consumed, g.		Produced, g.	
Mixed di*iso*butylene	100	1 : 2-Epoxy-2 : 4 : 4-trimethylpentane	53·5
Oxygen	39	Azeotrope of dimethylpentanone and 2 : 3-epoxy-2 : 4 : 4-trimethylpentane	15·6
		Low-boiling material (mainly *tert.*-butanol)	8·2
		High-boiling material (25% unsaturated alcohols, 20% glycols)	14·5
		Water and acids	19·2
		Carbon dioxide	14·0
		Volatile matter in effluent gas	9·8
		Unaccounted for	4·2
	139		139·0

A similar experiment with purified 2 : 4 : 4-trimethylpent-1-ene (in presence of aqueous disodium hydrogen phosphate as buffer) gave dimethylpentanone (11%), 1 : 2-epoxide (48%), and high-boiling residue (10%). The recovered olefin was substantially free from β-isomer, and no 2 : 3-epoxide was formed; hence no isomerisation occurred during oxidation.

Since the oxidation of di*iso*butylene was not carried to completion, unchanged olefin was recovered from the product. This could be re-used for fresh oxidations with sodium vanadate catalyst in the normal way. When attempts were made to re-use the recovered olefin with cobalt catalyst at high pH (>7), an unexplained retardation was repeatedly observed after oxidation had proceeded normally for about 1·5 hr. This effect occurred even when the olefin had been carefully washed and fractionated. It could be prevented by lowering the pH to 6—7.

The oxidation of purified 2 : 4 : 4-trimethylpent-2-ene was also investigated. Some small-scale experiments in glass at 90° with oxygen at atmospheric pressure, and in the presence of magnesia, showed that in the absence of a catalyst there was a long induction period, but that addition of a small amount of cobalt naphthenate or benzoyl peroxide initiated an immediate absorption of oxygen. Epoxide was detected in the product, but analytical difficulties (see below) prevented a quantitative assessment. The peroxide-initiated reaction led to more peroxidic products, mainly *tert.*-butyl hydroperoxide, than did oxidation of 2 : 4 : 4-trimethylpent-1-ene.

Oxidation of 2 : 4 : 4-trimethylpent-2-ene under pressure (200 lb./sq. in.) in the stainless-steel vessel at 130—140° (2·5 hr.) in presence of magnesium oxide gave a product in which the following were identified: unchanged 2 : 4 : 4-trimethylpent-2-ene (no -1-ene was detected), (?) *iso*butaldehyde, *tert.*-butanol, 4 : 4-dimethylpentan-2-one, 2 : 3-epoxy-2 : 4 : 4-trimethylpentane (25—26% yield), 2 : 4 : 4-trimethylpent-1-en-3-ol, and higher-boiling material probably containing diketones and 2 : 4 : 4-trimethylpentane-2 : 3-diol. By treatment with 2 : 4-dinitrophenylhydrazine in alcoholic sulphuric acid, a red derivative, m. p. 202—203°, was obtained from one of the higher fractions: this was identical with 2 : 4 : 4-trimethylpent-2-en-1-al 2 : 4-dinitrophenylhydrazone (Hadley, Hall, Heap, and Jacobs, *J.*, 1954, 1416), and it is probably also identical with Hickinbottom's presumed *tert.*-butylpyrazoline (*J.*, 1949, 287). The nature of the high-boiling product giving rise to this unsaturated hydrazone is uncertain; it may be 1 : 2-epoxy-2 : 4 : 4-trimethylpentan-3-ol (II), as a possible precursor (2 : 4 : 4-trimethylpent-1-en-3-ol; I) of this is present in the oxidate:

$$\mathrm{HO{\cdot}CHBu^t{\cdot}CMe{:}CH_2} \longrightarrow \mathrm{HO{\cdot}CHBu^t{\cdot}}\underbrace{\mathrm{CMe{\cdot}CH_2}}_{\mathrm{O}} \longrightarrow \mathrm{CHBu^t{:}CMe{\cdot}CH{:}N{\cdot}NH{\cdot}C_6H_3(NO_2)_2}$$

(I) (II) (III)

A subsequent oxygenation under similar conditions, but with sodium vanadate catalyst and aqueous sodium carbonate as base, gave a 53% yield of the isolated 2 : 3-epoxide.

Analysis of the Epoxides.—The epoxides were purified by further fractionation, and a sample of 1 : 2-epoxide obtained by this means was shown by freezing-point observations to be over 99·5% pure. Unexpected difficulty was encountered in assaying the purity of these epoxides by functional-group analysis by any of the conventional procedures. For example, Nicolet and Poulter's method (*J. Amer. Chem. Soc.*, 1930, **52**, 1186; Swern *et al.*, *Anal. Chem.*, 1947, **19**, 414) using hydrogen chloride in ether, applied without special precautions, gave only 79% of the expected titration on a pure sample. Furthermore, when applied to mixed products it gave unreproducible results. When this work was started, no cases of failure of the method had been recorded, although Hickinbottom and Wood (*J.*, 1951, 1601) have since reported that 1 : 2-epoxy-4 : 4-dimethyl-2-*neo*pentylpentane gives no titration at all.

Since a reliable quantitative method was desirable, Nicolet and Poulter's method as applied to the 1 : 2-epoxide was further investigated. It was found that factors such as the concentration of the sodium hydroxide used for titration, the freshness of the ether, and the order of mixing reagents all affected the result. The procedure was therefore modified (see p. 2168), and, if rigidly adhered to, it could then give 95% of the expected figure.

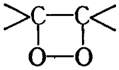
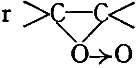
Various other published procedures for estimating epoxides, such as those based on interaction with magnesium chloride (Lubatti, *J. Soc. Chem. Ind.*, 1932, **51**, 361T), hydrochloric acid in dioxan (King, *Nature*, 1949, **164**, 706), or sodium thiosulphate (Ross, *J.*, 1950, 2270), gave valueless results. Oxidation with periodic acid gave a very approximate estimate (10% low), although sodium periodate (cf. Hirst and Jones, *J.*, 1949, 1659), either in aqueous or in *iso*propanol solution, gave quite unreproducible results.

The failure of these methods is understandable in view of the ready isomerisation of the 1 : 2-epoxide, especially in acid medium. An examination of the products of interaction of the 1 : 2-epoxide with hydrogen chloride (Part III, *loc. cit.*, p. 2186) showed that, besides the chlorohydrin, trimethylpentanal was formed, and further that the chlorohydrin readily lost hydrogen chloride.

An analytical method was finally developed based on reaction of the epoxide with dibutylamine. This gave results closely agreeing with the value expected from physical methods, although reproducibility was not high (standard error for a single determination up to 1·3%), and the procedure was too lengthy for a routine method.

No satisfactory chemical method for estimating the 2 : 3-epoxide was found at all, as it gave only a fraction of the expected titration by any of the methods mentioned (the dibutylamine method was not tried).

Once a pure reference sample was obtained, fairly pure samples of the 1 : 2- or 2 : 3-epoxides could be assayed by infra-red spectroscopy, but the absence of any strong absorption bands precluded the spectroscopic estimation of epoxides in mixed products. All yields quoted in this paper, unless otherwise stated, refer to isolated material corrected for impurity by spectroscopic measurement.

Mechanism of Epoxidation.—We have not been able to obtain any direct evidence as to the mechanism of this interesting reaction. Current theory of autoxidation postulates that the initial attack consists of the removal of the least strongly bound hydrogen atom. On this basis, attack at the 3-position in the 2 : 4 : 4-trimethylpent-1-ene molecule would be expected, but in fact very little product that is unequivocally formed by this route has been obtained. Since over 50% yields of epoxide can be isolated, and much of the residual product (diol, dimeric condensation products, and probably dimethylpentanone) appears to be derived from epoxide which has undergone further reaction, any mechanism based on initial formation of a 3-hydroperoxide which later oxidises a further molecule of olefin to epoxide is unlikely or at least will be incomplete. Paquot (*op. cit.*) revives the old theory of direct addition of oxygen to the double bond to give a cyclic peroxide,  $>\underset{|}{C}-\underset{|}{C}<$ ($O-O$) or  $>C-C<$ ($O\rightarrow O$). Although the existence of such peroxides has never been proved, it is difficult to escape the conclusion that in the present case the initial attack upon the olefin is mainly at the double bond. On this view, the unsaturated alcohols in which a hydroxyl group has entered at the 1- or the 3-position are the products of side-reactions. A parallel may be drawn with the action of chromium trioxide in acetic anhydride, which normally attacks the carbon atom in the allyl position (Treibs and Schmidt, *Ber.*, 1928, **61**, 459), but with 2 : 4 : 4-trimethylpent-1-ene yields the epoxide as main product (Byers and Hickinbottom, *J.*, 1948, 1334; cf. also Hickinbottom and Wood, *loc. cit.*).

The oxidation herein described has characteristics (autocatalytic and inhibition effects) of a radical-chain reaction, and on this basis may be presumed to be homopolar. This is in contrast to epoxidation by means of peracids, which shows normal kinetics and appears to be heteropolar (Swern, *J. Amer. Chem. Soc.*, 1947, **69**, 1692). Here again the precise mechanism is still uncertain, the most plausible explanation being that advanced by Criegee (*Fortschr. Chem. Forsch.*, 1950, **1**, 550), envisaging addition of a hydroxyl cation followed by elimination of a proton.

EXPERIMENTAL

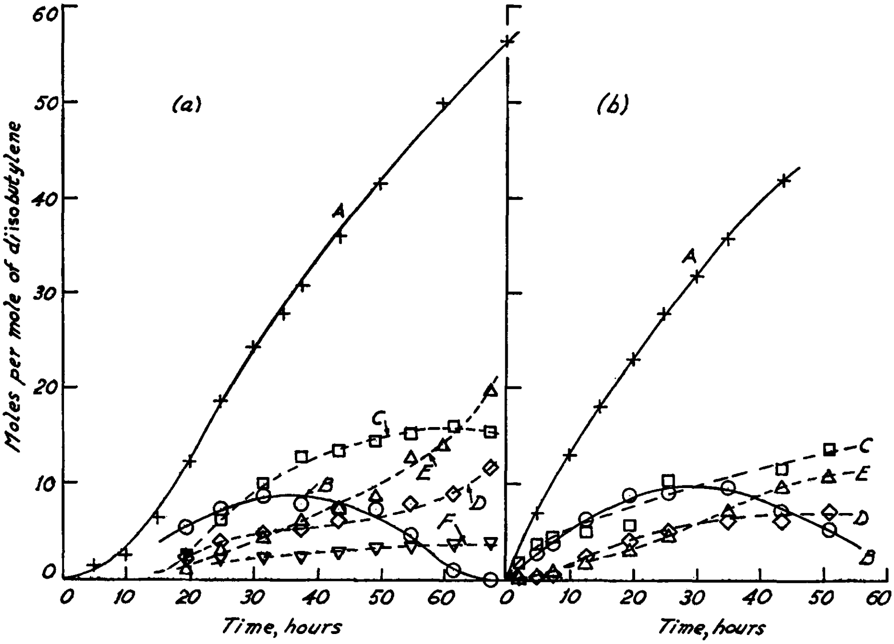
Materials.—The di*iso*butylene used was mainly the equilibrium mixture of isomers [80% of 2 : 4 : 4-trimethylpent-1-ene (" α "), 20% of -2-ene (" β ")], but a few experiments were carried out with material enriched in the α-isomer by fractional distillation, and also on the pure isomers.

The commercial olefin was obtained from two sources, (i) a crude polymerisate from Anglo-Iranian Oil Co. Ltd., from which di*iso*butylene was separated by distillation, (ii) a purified di*iso*butylene, of U.S. origin, substantially free from other hydrocarbons but containing an oxidation inhibitor. In order to obtain consistent results it was necessary to distil the latter material before use.

With few exceptions, the oxidations were catalysed by heavy-metal salts, added as the oilsoluble naphthenates (" Novenates "; A. Boake Roberts & Co.), normally at 0·1% w/v on the olefin.

Oxidation of 2 : 4 : 4-*Trimethylpent*-1-*ene in Glass Apparatus with Oxygen at Atmospheric Pressure.*—Freshly distilled 2 : 4 : 4-trimethylpent-1-ene (213 g.) was agitated in oxygen, by means of a " recycle " stirrer, in a flask immersed in a bath at 90—95°. Samples were withdrawn at 6-hourly intervals for titration. The progress of the experiments is summarised in Figs. 1*a* and 1*b*. Distillation of the final oxidate gave formic acid, water, formic esters, 4 : 4-dimethylpentan-2-one, b. p. 70°/150 mm. (semicarbazone, m. p. 176°, undepressed by an authentic specimen), 2 : 4 : 4-trimethylpentane-1 : 2-diol, m. p. 62—63° (not depressed by an authentic specimen), and a substance, b. p. 66—67°/2 mm., n_D^{20} 1·4438, *M* (in camphor) 251, which was apparently a bimolecular condensation product of the epoxide (cf. Hickinbottom, *J.*, 1948, 1328, 1331, and Part III).

FIG. 1. *Oxidation of* 2 : 4 : 4-*trimethylpent*-1-*ene at atmospheric pressure in absence of alkali,* (*a*) *without catalyst,* (*b*) *with* 0·1% *of cobalt naphthenate. A, oxygen absorbed; B, epoxide formed; C, carbonyl compounds formed; D, acids formed; E, esters formed; F, peroxides formed.*



Oxidation of Diisobutylene in a Steel Vessel with Air under Pressure.—Apparatus. The reaction vessel and its fittings were constructed of FDP stainless steel. The vessel consisted of a cylinder, 10 cm. in diameter and about 30 cm. long. with flanged ends, with a total capacity of *ca.* 2·1 l. It was heated electrically by a winding carrying 5 amp. at 230 v, and was equipped with a Kestner turbo-type stirrer, 5 cm. in diameter, rotating at *ca.* 1400 r.p.m. Through the bottom flange passed pipes for the air supply (immediately under the stirrer), and for the withdrawal and sampling of the product. Through the top flange passed the gas exit line, the reflux return line, and a thermometer pocket. The air was supplied from storage tanks at 300 lb./sq. in., and the pressure in the reaction vessel was kept constant by means of a reducing valve on the inlet side; air flow *into* the vessel was not measured. The exit gases passed down a water-cooled coil condenser, and then through a gas-liquid separator, the liquid reflux being returned to the vessel through a U-bend. The gases passed on and were reduced to atmospheric pressure through a hand-controlled needle-valve, kept warm to avoid condensation and freezing-up; the rate of flow through the apparatus was controlled entirely by this valve. The gas at atmospheric pressure was passed through a capillary flowmeter and wet gas-meter, but in advance of the flowmeter a very small proportion of the gas was drawn off to an oxygen meter. The alkali solution was pumped into the vessel from a measuring tank *via* an entry into the reflux-return line at the top of one arm of the U. The vessel was charged through the thermometer pocket.

Catalysed oxidation in absence of alkali. Di*iso*butylene (1070 g., 9·5 moles; containing *ca.* 90% of α-isomer) containing 0·1% of cobalt naphthenate was oxidised with air at *ca.* 120° and under 200 lb./sq. in. pressure. The air rate was such that the effluent gas rate was 120 l./hr., the oxygen being completely absorbed. About 12—14 moles of oxygen were absorbed during 14·5 hr. The product (1224 g.) was extracted with aqueous sodium carbonate, and this was extracted with 200 ml. of di*iso*butylene, which was added to the acid-free oxidate. This was then distilled, leaving some 4—5% of tarry residue. The fractions, b. p. 80—94°/6—7 mm., deposited 65 g. of 2 : 4 : 4-trimethylpentane-1 : 2-diol, m. p. 61° after recrystallisation. The liquid portion of the distillates was refractionated to give (percentages are of crude product): (i) b. p. 52—67° (1·1%; acetone and some formaldehyde), (ii) 67—80° (1·6%), (iii) 80—85° (3·3%; *tert.*-butanol), (iv) 85—120° (16%; di*iso*butylene and water), (v) 120—130° (18·5%; 4 : 4-dimethylpentan-1-one), (vi) 130°/760—101°/14 mm. (14·55%), (vii) 101—102°/14 mm. (2·75%), (viii) 102—116°/14 mm. (7·1%). Fraction (iv) was equivalent to the di*iso*butylene used for extraction, and hence the amount of olefin unchanged from the oxidation was nil. Fraction (vii) was about 65% of 2 : 4 : 4-trimethylpentane-1 : 2-diol formate; from it were obtained by hydrolysis with alcoholic potash a further 12·2 g. of the free diol, and potassium formate. Fraction (viii) was mainly cyclic condensation product. With an alcoholic sulphuric acid solution of dinitrophenylhydrazine it gave 2 : 4 : 4-trimethylpentanal dinitrophenylhydrazone, m. p. 163°. The major single compound obtained in this oxidation was trimethylpentanone (yield *ca.* 20% of theory), and the total yield of free and esterified diol was 5%.

Oxidation in the presence of aqueous sodium carbonate. The solution of sodium carbonate was pumped in during the oxidation at such a rate that the pH limits of the aqueous layer were 7—8·5. Details of a typical experiment are as follows. The reaction vessel was charged with di*iso*butylene (80% of α-isomer; 1075 g., 9·6 moles) and cobalt naphthenate (1·5 g.), and the pressure raised with air to 100 lb./sq. in. The vessel was heated, with stirring, and when the temperature reached 130° the pressure was raised to 200 lb./sq. in. and the exit valve was opened slightly so as to give an effluent gas rate of 50—60 l./hr. Heating was continued until the temperature reached 140° (a further 5 min. approximately), whereat it was kept for the duration of the run. Once the oxidation was proceeding, no further application of heat was necessary, and indeed it was often necessary to apply slight cooling (by means of an air-jet). The alkali feed (16% aqueous sodium carbonate) was started, at *ca.* 70—75 ml./hr., about 5 min. after the start of the air flow, but if the oxidation was slow in commencing, the alkali feed was stopped again so as to keep the pH below 9. The oxygen content of the effluent gas dropped as absorption started, and when it reached 5% (usually in 10—30 min. after the start of the air flow) the effluent rate was increased to 180 l./hr. The oxygen content rapidly fell to 0—1% and remained at this level for the duration of the oxidation. Small samples were withdrawn frequently (every 15—30 min.), and the pH of the aqueous layer was determined by spotting on a tile with B.D.H. Universal Indicator. The pH was kept as far as possible at 8—8·5 by suitable adjustment of the alkali feed; normally it settled down at this value without any difficulty, and it was only at the start of an oxidation that any wider variation was liable to occur. After 4 hr. the inlet and outlet gas valves and the alkali feed were closed. The oxidate was allowed to cool to 40° before being discharged from the vessel, or else was passed out through a water-cooled condenser. The product formed a dark brown aqueous layer and a yellow-to-orange upper layer. There was a small amount of dark interfacial sludge (less when sodium vanadate catalyst was used), but the separation of the phases was quite clean.

290 ml. of alkali (equivalent to 53 g. of sodium carbonate) were used. The effluent gas totalled 770 l., and the oxygen absorbed was estimated to be 180 l. (5·2 moles). The product consisted of 990 g. of organic and 407 g. of aqueous phase, hence the aqueous layer had increased in weight by 70 g.

Distillation of the organic phase through an insulated column, 50 × 2·5 cm. (internal), packed with glass helices, at a reflux ratio of 10 : 1, gave (i) b. p. up to 65°/125 mm. (450 g.), (ii) 65°/125—70°/100 mm. (112 g.), (iii) 70—77°/100 mm. (332 g.), and residue (66 g.). Fraction (i), plus the contents of the cold-trap, was washed thrice with water, to give 419 g. of substantially unchanged di*iso*butylene. The olefin consumed was therefore 656 g., so that conversion was 61%. Fraction (iii) was 90—95% 1 : 2-epoxy-2 : 4 : 4-trimethylpentane, so the yield of epoxide was 50—53% on olefin consumed.

The oxidation time was reduced progressively to 2 hr., without appreciably affecting the degree of conversion, by increasing the effluent gas rate (finally to 360 l./hr.), the alkali feed being increased correspondingly. The oxidation proceeded smoothly, and the yields of 1 : 2-epoxide fraction did not alter.

Oxidations were carried out in presence of 0·1—1·0% (overall) of cobalt, manganese, lead, or ferric naphthenate, or sodium vanadate or tungstate dissolved in the alkali feed; in all cases the yield was 51—56% of 1 : 2-epoxide (based on olefin consumed). When no catalyst was added, the vessel (but not the rest of the apparatus) having previously been thoroughly washed out, the yield was 50%.

Some 25% of the distillation residue from the epoxide was composed of unsaturated alcohols. The 2 : 4-dinitrobenzoates of 2 : 4 : 4-trimethylpent-1-en-3-ol (m. p. 118°) and 2-*neo*pentylprop-2-en-1-ol (m. p. 54·5°; cf. Part II, p. 2176) were obtained from fractions of b. p. up to 82°/19 mm. In addition, periodate analysis showed the presence of approximately 20% of glycols, presumably mainly 2 : 4 : 4-trimethylpentane-1 : 2-diol.

The acidic products obtained in the presence of alkali appeared to be similar to those obtained in its absence. Acidification of 10 l. of the alkaline aqueous layer from several oxidations, followed by steam-distillation, gave only about 50 g. of water-insoluble mixed carboxylic acids, b. p. *ca.* 150—220°. The main component seemed to be ββ-dimethylbutyric acid, but from the b. p. it was probable that smaller amounts of pivalic and αγγ-trimethylvaleric acids were also present. The steam-distillate contained in addition 26·5 g. of water-soluble aicds (calculated as formic).

Similar results were obtained by oxidation in presence of magnesium oxide, added to the charge (50 g. to 1075 g. of olefin) either dry or suspended in water. Disodium hydrogen phosphate alone was insufficient to maintain the pH unless sodium hydroxide was pumped in during the oxidation. In this way, 1040 g. of purified α-isomer (more than 99% of 2 : 4 : 4-trimethylpent-1-ene), 1·5 g. of cobalt naphthenate, and 25 g. of $Na_2HPO_4,12H_2O$ in 100 ml. of water, subsequently kept at pH 8—8·5, yielded unchanged hydrocarbon (39·2%), 4 : 4-dimethylpentan-2-one (10% yield on olefin consumed), 1 : 2-epoxide (48%), and residue (10 wt. %). Less than 0·2% of 2 : 3-epoxide was detected.

An oxidation in presence of solid potassium hydroxide (cf. Bost and Lockhart, *loc. cit.*) gave neither epoxide nor carbonyl compounds detectable by analysis.

Later, oxidations were carried out on a larger scale in a 27-l. mild-steel vessel; induction periods and oxidation rates were less reproducible in this apparatus.

Oxidation of 2 : 4 : 4-*Trimethylpent*-2-*ene*.—Preliminary experiments were carried out in glass apparatus as described above. The peroxidic product was shown (G. W. Godin and J. L. Benton, unpublished work in these laboratories) to be mainly *tert.*-butyl hydroperoxide, isolated through the sodium salt and identified by infra-red spectrum.

Later experiments were carried out in the stainless-steel vessel as described above.

(*a*) 2 : 4 : 4-Trimethylpent-2-ene (911 g., 8·13 moles), magnesium oxide (35 g.), and cobalt naphthenate (1·5 g.) were oxygenated with air at 130—140° for 1·5 hr. [about 4·3 moles of oxygen (137 g.) had been introduced]. 947 G. of product (including magnesia) were recovered, therefore 136 g. had been lost as carbon dioxide and volatiles. After filtration, 730 g. of liquid product were obtained. Titration at this point showed peroxides less than 0·6% (as Bu^tO_2H). It was distilled through a 75-cm. column packed with glass helices to give the following fractions :

Fraction	B. p./mm.	Weight, g.	n_D^{20}	Composition
(i)	55—58°/758	12·0	1·3732	Acetone, etc.
(ii)	58—65°/758	8·5	1·3805	Acetone, (?)*iso*butaldehyde, etc.
(iii)	65—76°/758	19·3	1·3966 *	*iso*Butaldehyde, etc.
(iv)	76—85°/758	65·8	1·3942	Mainly *tert.*-butanol
(v)	85—102°/758	18·0	1·4038	
(vi)	102—103°/758	12·0	1·4127	Unchanged olefin
(vii)	53—58·5°/129	245·0	1·4154	do.
(viii)	58·5—72°/129	17·0	1·4119	Olefin, epoxide (50%), dimethylpentanone
(ix)	72—73°/129	174·0	1·4081	2 : 3-Epoxide (95%)
(x)	58·5—60°/28	23·0	1·4189	2 : 3-Epoxide (30%)
(xi)	60—82°/19	22·5	1·4362	2 : 4 : 4-Trimethylpent-1-en-3-ol, 1 : 2-epoxy-2 : 4 : 4-trimethylpentan-3-ol (or 2 : 4 : 4-trimethylpent-2-enal), diketone, diol, etc.
(xii)	82—96°/19	18·5	1·4369	
(xiii)	96—110°/19	16·5	1·4425	
Residue		45·5	—	

* Two-phase azeotrope; only upper layer examined.

Acetone was identified in fractions (i) and (ii) by its dinitrophenylhydrazone. Both these fractions also contained a small amount of unidentified material insoluble in water. The evidence for *iso*butaldehyde in fractions (ii) and (iii) is not conclusive; dinitrophenylhydrazones were obtained from both which, after repeated recrystallisations from alcohol, melted at 180—

182° with previous softening below 170°; a mixed m. p. with the derivative of *iso*butaldehyde gave no depression of the final m. p. *tert.*-Butanol was identified as its phenylurethane. Infra-red examination showed that no isomer of 2 : 4 : 4-trimethylpent-2-ene was present in fractions (vi) and (vii), but they contained traces of ketones and alcohols. From fraction (viii) some 4 : 4-dimethylpentan-2-one was isolated as its dinitrophenylhydrazone. Fraction (xi) gave reactions for both carbonyl and hydroxyl. With alcoholic 2 : 4-dinitrophenylhydrazine containing sulphuric acid it gave a red derivative, m. p. 202—203° after recrystallisation. This was identical (mixed m. p.) with a sample of 2 : 4 : 4-trimethylpent-2-en-1-al dinitrophenylhydrazone (III) (Hadley *et al.*, *loc. cit.*). Fraction (xi) also gave a 3 : 5-dinitrobenzoate, which appeared to be a mixture. After repeated recrystallisation, its m. p. had risen from 62—66° to 108—110°, and the purified derivative gave no depression of m. p. in admixture with that of 2 : 4 : 4-trimethylpent-1-en-3-ol. From other higher fractions were isolated a dinitrobenzoate, m. p. 79—81°, apparently the impure bisdinitrobenzoate of a C_8 diol, and a dinitrophenylhydrazone, m. p. 254—256°, of analytical composition approximately that of the bisdinitrophenylhydrazone of a C_8 diketone. Besides the compounds already mentioned, there was evidence from titrations of small amounts of glycols and esters.

(*b*) 2 : 4 : 4-Trimethylpent-2-ene (1080 g.) was oxygenated at 140° with air at 200 lb./sq. in. for 2·5 hr. Meanwhile 15% sodium carbonate solution in which was dissolved 1·0% of vanadium pentoxide was pumped in to keep the pH at 8—9; 500 ml. in all were used. The effluent gas emerged at 300 l./hr., all oxygen having been absorbed. The oil phase of the product was distilled, and the fraction, b. p. 60—70°/100 mm. (46·9%; 53·5 wt. % of the olefin consumed), was estimated by infra-red measurements to be 100% pure 2 : 3-epoxy-2 : 4 : 4-trimethylpentane.

Properties of the Diisobutylene Oxides.—A redistilled sample of 1 : 2-epoxy-2 : 4 : 4-trimethylpentane, b. p. 75°/93 mm., n_D^{20} 1·4155, was estimated by f. p. to be 99·5% pure. 2 : 3-Epoxy-2 : 4 : 4-trimethylpentane, b. p. 66°/100 mm., n_D^{20} 1·4078, was similarly found to be 98% pure.

The following vapour-pressure data were observed :

Vapour pressure, mm.	49	50	73	74	99	100	150	200
	Temperature							
1 : 2-Epoxy-2 : 4 : 4-trimethylpentane	—	61·6°	—	70·4°	—	77·4°	98·7°	95·5°
4 : 4-Dimethylpentan-2-one	49·2°	—	57·9°	—	65·0°	—	—	83·0
Azeotrope of dimethylpentanone and 2 : 3-epoxide	—	49·8	58·0	—	65·2	—	75·0	83·0

It appears that the dimethylpentanone was slightly impure, and its true b. p. is slightly higher than that of the azeotrope.

Fractions containing the two epoxides and 4 : 4-dimethylpentan-2-one were estimated by infra-red spectroscopy by the method of matching mixtures, in order to obviate the small error caused by the overlapping of bands. Maxima at 883 and 901 cm.$^{-1}$ were found to be characteristic of 1 : 2- and 2 : 3-epoxy-2 : 4 : 4-trimethylpentane respectively, and further maxima at 958 and 1253 cm.$^{-1}$ provided key points for the matching. The ketone can be matched by a band at 1151 cm.$^{-1}$, although the carbonyl absorption gives a more sensitive test for its presence. The absorption curves of the two epoxides are shown in Fig. 2.

Functional-group Analysis of 1 : 2-*Epoxy*-2 : 4 : 4-*trimethylpentane.*—*Ethereal hydrogen chloride method.* A statistically-planned investigation of the method (Swern *et al.*, *loc. cit.*) showed that the following factors all had a significant effect on the result : molar ratio hydrogen chloride : epoxide, dilution of the sample before addition, and order of addition of the reagents, the first two not being independent. The amount of agitation during mixing, and increasing the time of reaction from 30 to 90 min., made no significant difference. Diluting the blank (*i.e.*, reagents without epoxide sample) with ether increased the titration by an amount depending on the order of addition.

The following procedure, rigidly followed, gave a mean result of 94·25% of the true amount, with a standard error for a single determination of 0·53%. To 10 ml. of approx. 0·6N-hydrogen chloride in ether in an iodine flask was added with swirling a solution of about 0·4 g. of epoxide in 10 ml. of ether. This was set aside, stoppered, for 30 min. Then 30 ml. of 0·015% alcoholic α-naphtholphthalein were added, and the contents were titrated with 0·2N-sodium hydroxide to an end-point not fading in 15 sec. A blank determination was carried out in exactly the same way, but with omission of the epoxide.

Blank titrations on the same materials drifted with time, apparently depending on fluctuations in the ambient temperature. Hence it would be better to run blanks simultaneously with each sample. The presence of 0·5% of sulphuric acid in the reagent (this is 31% of the hydrogen chloride content) caused results to be 13% lower than otherwise.

Periodate method. The method described in *J.*, 1949, 2998 (*Note :* " iodate " is a misprint for " periodate ") was applied, by shaking the sample with the acid periodate in a stoppered flask for 30 min. Pure 1 : 2-epoxide had an apparent purity of 90% by this method.

Dibutylamine method. About 0·2 g. of epoxide was weighed into a clean, dry, glass tube of about 6 mm. internal diameter, 30 cm. long, and 1 mm. wall thickness, closed at one end. It was washed in with 1·25 ml. of methanol, and 0·5 ml. of di-*n*-butylamine and 0·4 ml. of water (all fairly accurately measured) added. The tube was sealed, the contents mixed, and the tube heated for 2 hr. in a steam pressure-vessel at 200 lb./sq. in. After cooling, the tube was opened and the contents were poured into a test-tube and washed in with 10 ml. of acetic anhydride in several portions. After mixing, the solution was heated at 55° for 1·5 hr. with exclusion of moisture. A blank determination was run, the epoxide being omitted. At this point, 10 ml. of acetic acid were added to the blank only. After addition of one drop of 0·5% metanil-yellow in acetic anhydride containing 2% of acetic acid, the blank was titrated with 0·1N-perchloric acid in acetic acid until the colour was just changing from reddish-brown to purple. This titration should not exceed 0·2 ml. The sample was then similarly titrated to match the blank, and the difference between the two titrations was the equivalent of the *tert.*-amine formed and hence of the epoxide.

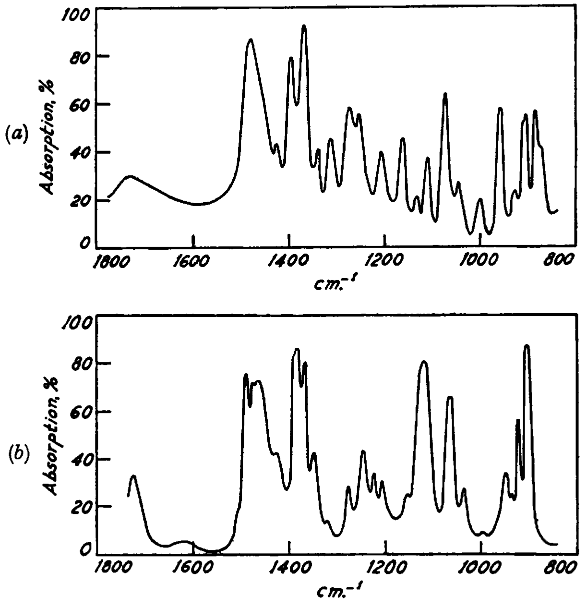


FIG. 2. *Infra-red absorption spectra of* (*a*) 1 : 2-*epoxy*-2 : 4 : 4-*trimethylpentane,* (*b*) 2 : 3-*epoxy*-2 : 4 : 4-*trimethylpentane.*

A sample analysed thus gave 100·35% of epoxide, as the mean of 24 results, with a standard error of a single determination of 1·31%. The same sample analysed by f. p.-measurement was found to be 99·0 ± 0·5 mol. % pure.

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