22. *The Course of Autoxidation Reactions in Polyisoprenes and Allied Compounds. Part I. The Structure and Reactive Tendencies of the Peroxides of Simple Olefins.*

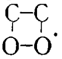
By Ernest Harold Farmer and Alvappillai Sundralingam.

Criegee's conclusion that the peroxide formed by the interaction of molecular oxygen with *cyclo*hexene is a hydroperoxide in which the olefinic unsaturation survives is confirmed. The peroxides formed similarly from 1-methyl- and 1 : 2-dimethyl-*cyclo*hexene are also olefin hydroperoxides. The formation of hydroperoxides from olefins and unconjugated polyolefins in general is one of a group of important olefinic reactivities due to the lability of the hydrogen atoms of methylene groups in the α-position to the double bonds.

The hydroperoxide groups decompose spontaneously, and also by the action of heat, giving (*a*) cyclic epoxides and alcohols, (*b*) oxidation products, and (*c*) oxygenated polymeric products. In this decomposition the hydroperoxide groups act as active oxidising agents, attacking the carbon chain at the double bond, themselves reverting to hydroxyl groups. Ketones are not formed in recognisable amounts by the spontaneous decomposition of the cyclic hydroperoxides, although they have long been known to appear among the autoxidation products of mono-olefinic terpenes; they are formed, however, to a considerable extent by the violent decomposition promoted by an organic ferrous salt.

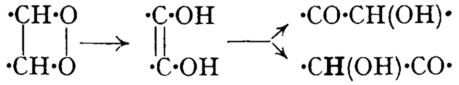
The decomposition of the olefin hydroperoxides by sulphuric acid, by superheated water, and by alkali has been examined in some detail, the first two reagents causing extensive oxidation of the carbon chain, and the last extensive hydrolysis of the hydroperoxide together with some oxidation. The nature of the products obtained in the sulphuric acid decomposition suggests a reason for the strong promoting influence of organic acids when present during olefin autoxidations.

The mechanisms of the hydroperoxide decompositions and of the complementary oxidation reactions are considered; also the manner of formation of the polymeric products, which doubtless involves the same fundamental reactivities as are involved in the drying of unsaturated oils.

The structural changes which occur in olefinic substances when they undergo oxidation by molecular oxygen have never been elucidated, although many of these changes, such as the autoxidation of drying oils and of rubber, are of enormous practical importance. It has commonly been supposed that absorption of molecular oxygen occurs at some or all of the ethylenic centres to give peroxidic groupings, which, for want of a better representation and following Engler's suggestion (*Ber.*, 1897, **30**, 1669; 1898, **31**, 3046; 1900, **33**, 1090), have been formulated as cyclic structures  $\begin{matrix}C-C\\ | \quad |\\ O-O\end{matrix}$. There is, however, little direct evidence supporting such a formulation beyond (1) that the unsaturation of the autoxidised substance usually decreases progressively (although not in quantitative correspondence) as oxygen-intake increases, and (2) that frequently the reaction ends in hydroxylation of the double bond to yield a 1 : 2-glycol, or in complete scission of the carbon chain at the double bond. The peroxidic groupings, as is well attested, show a tendency to decay, with formation from the peroxidised olefin of one or more of a wide variety of oxygenated materials, including olefin oxides, ketones, glycols, ketols, miscellaneous oxygenated materials of unknown structure (but important in the drying oils, since they seem to be largely responsible for the formation of films and skins), and, as the result of chain-scission, aldehydes, ketones, carboxylic acids, and hydroxy-carboxylic acids. If it be assumed that all these types of product, as well as certain simple degradation products such as water, carbon dioxide, and the lower fatty acids, arise from simple peroxides of the original olefins, it becomes difficult on the basis of present information to fit them into a coherent scheme and to reconcile many apparently discordant observations.

In attempting to devise such a scheme, consideration must necessarily be given to the effect on the course of reaction of the somewhat varied ways in which the autoxidations can be promoted and the conditions under which they are conducted. The most important influences seem to be catalytic agents or agencies and the temperature conditions. Many different organic, inorganic, and metallic catalysts, as well as light of different wave-lengths, have been used to initiate and facilitate autoxidation, and it is to be noted that the manner of their application may have important effects on the final products; also, raising the temperature above room-temperature is recognised generally to accelerate reaction. Whether either catalytic influences or the conditions of reaction can ever influence the character of the primary oxidation reactions (as distinct from controlling the purely secondary autoxidative changes), however, is not known with certainty. In most autoxidation reactions it is fairly clear that reaction begins with the absorption of oxygen and the immediate production of peroxide groups; in other reactions the participation of peroxides is not so obvious (since no peroxides survive) but is commonly accepted as a primary feature of the reaction mechanism. A contrary view is, however, still sometimes expressed, and fairly recently Szent-Györgyi concluded that by the influence of a specific type of chemical catalyst the absorption of oxygen can lead directly, without intervention of peroxides, to the formation of olefin oxides (*Biochem. Z.*, 1924, **146**, 246).

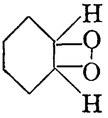
The view that autoxidation occurring at olefinic centres leads first to the formation of cyclic peroxide groups, then to that of oxido-groups and later to glycols or products of chain scission, has often been expressed, although it could not be established as a *general* course of reaction in view of innumerable observations to the contrary. Ellis (*Biochem. J.*, 1936, **30**, 753) obtained yields of crystalline oxido-compounds as high as 15% from elaidic and oleic acids, as well as considerable yields of obviously chain-scission products. An alternative, however, to the cyclic peroxide–oxide–glycol–scission product sequence has been postulated by Willstätter and Sonnenfeld (*Ber.*, 1913, **46**, 2952), which seems to be accepted by most recent writers on the autoxidative changes occurring in vegetable oils (*e.g.*, Ellis, *J. Soc. Chem. Ind.*, 1926, **44**, 401T; Morrell and Marks, *J. Oil Colour Chem.*, 1927, **10**, 186; 1929, **12**, 183; Long and McCarter, *Ind. Eng. Chem.*, 1931, **23**, 786). This holds that the cyclic peroxide groups formed in the first stage of oxidation have the ability to isomerise to the corresponding unsaturated diol or its tautomeric ketol:



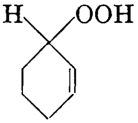
and would mean, if it were correct, that there is a direct and very simple path connecting the initia formation of a peroxide group with the final occurrence of chain scission at the original double bond, since the unsaturated enol might well be deemed to be susceptible to further oxidative attack culminating in scission. The hypothesis, however, fails completely to make any provision for the undoubted formation in some autoxidations of oxido-compounds and saturated 1 : 2-glycols, or indeed for the occurrence of secondary autoxidative change at all in peroxides derived from the substituted system $\cdot CR\colon CR'\cdot$ (R, R$'$ = alkyl), since such peroxides would be structurally incapable of giving ketol tautomerides. It is the object of this and subsequent papers to examine various aspects of the autoxidation problem as it affects simple and high-molecular unconjugated * olefinic substances with a view to trace the main and subsidiary changes and to correlate these with certain other types of oxidative reaction to which olefinic substances are susceptible.

In 1928 Stephens (*J. Amer. Chem. Soc.*, **50**, 568) discovered that *cyclo*hexene, when treated with oxygen in daylight, gave a liquid peroxide, $C_6H_{10}O_2$, presumed to be a double-bond adduct (I), which could be isolated by distillation. In 1936 one of us (with E. S. Narracott), in the course of preliminary experiments on the oxidation of rubber, found that when commercial xylene was used as solvent and an organic cobalt salt as catalyst, the xylene underwent slow oxidation with production of tolualdehyde, *m*- and *p*-toluic acid, and an alcohol which was doubtless toluic alcohol (see Note, this vol., p. 185). This was one of a number of interesting examples, which it is hoped to discuss later elsewhere, of the strong reactivity of methylene groups situated in the α-position to olefinic double bonds—a reactivity involving replacement or separation of hydrogen atoms. On the assumption that the formation of a peroxide group is the first step in the oxidation by molecular oxygen, the primary oxidation product of xylene must have been a hydroperoxide, $CH_3\cdot C_6H_4\cdot CH_2\cdot OOH$, comparable with Rieche's monoalkyl peroxides, and it was of great significance, as reflecting the relative natural tendencies towards displacement of olefinic and methylenic hydrogen atoms in the system $\cdot CH{:}CH\cdot CH_2\cdot$ (at least in certain types of reactivity), that in xylene the usual aromatic replaceability of nuclear hydrogen is actually superseded by replaceability of α-methylenic hydrogen atoms. α-Methylenic reactivity, as distinct from ordinary double-bond additivity, appears indeed to be potentially important in the chemistry of most mono-olefinic and unconjugated polyolefinic compounds, and especially is this true of the latter, since in many of these, owing to the multiple unsaturation, the mobility of α-methylenic hydrogen seems to be enhanced.

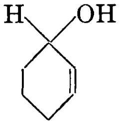
Stephens's peroxide was re-examined by Hock (Hock and Schräder, *Naturwiss.*, 1936, **24**, 159; *Angew. Chem.*, 1936, **49**, 595; Hock, *Oel u. Kohle*, 1937, **13**, 697), who obtained certain interesting results as regards the reactivity of the peroxide (see below) but agreed with Stephens's formulation of the peroxide as the double-bond adduct (I). Our own examination of *cyclo*hexene peroxide, begun in 1939 with the object of throwing light on a number of perplexing observations made over several years of study of the autoxidation and general reactivity of rubber, was forestalled in an important respect by Criegee, Pilz, and Flygare (*Ber.*, 1939, **72**, 1799), who showed that the peroxide formed from *cyclo*hexene in ultra-violet light must be a hydroperoxide (II) still containing a double bond, since (1) it is reducible by sodium sulphite to *cyclo*hexen-3-ol (III), (2) it absorbs 1 mol. of bromine per mol., and (3) it contains one atom of active hydrogen per mol. This confirmed the above-mentioned indications of the importance of α-methylenic reactivity in the chemistry of olefinic systems and rendered desirable further investigation, especially of the secondary autoxidation processes, of *cyclo*hexene and other allied olefins.



(I.)



(II.)



(III.)

Point of Oxidative Attack.

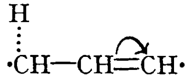
In numerous oxidations of carefully purified *cyclo*hexene, carried out by us in quartz flasks in the radiation from a mercury-vapour lamp, there was usually formed in 2—4 hours at temperatures between 30° and 40° about 30—40% of oxygenated material containing about 80% of monomeric peroxide, as determined both by direct estimation of peroxidic oxygen and by isolation of the pure peroxide by fractional distillation at greatly reduced pressure. The peroxide thus isolated behaved exactly as described by Criegee in regard to unsaturation, active hydrogen content, and reducibility to *cyclo*hexenol, and also was quantitatively reducible by hydrogen and platinum to crystallisable *cyclo*hexanol, and not to *cyclo*hexane-1 : 2-diol. Hence, peroxide formation in itself involved none of the reduction of unsaturation which must result from any addition of oxygen to the original double bond : on the contrary, oxidative attack was here confirmed to affect in the primary reaction only the α-methylene groups. The mode of attack, involving displacement of a methylenic hydrogen atom, is doubtless similar to that occurring in the peroxidation of saturated hydrocarbons, although the process is enormously facilitated in olefinic substances by an enhanced tendency to dissociation of hydrogen promoted apparently (in spite of the fact that the dissociation is probably of free-radical rather than of ionic character) by normal electronic dis-

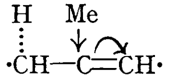
---

* Owing to the difference in structure between conjugated and unconjugated olefins, the course of autoxidative reaction in the two cases must necessarily differ considerably, although certain features will be similar.

placements in the double-bonded system (IV); furthermore the attack is found to be accelerated, as might perhaps be expected, if an inductively-acting alkyl group is attached to the ethylenic carbon atom adjacent to the methylene group (system V), as occurring in trimethylethylene or 1-methyl*cyclo*hexene. In the general case, therefore, although any α-methylene group is a potential reactive centre, the most likely point of attack where several such groups are present may be expected to be that one in which the tendency to dissociation of hydrogen will be most facilitated by normal electronic polarisation. Hence, although attack is possible at either of the methylene groups in the unsubstituted system $\cdot\text{CH}_2\text{·CH:CH·CH}_2\cdot$, it is most likely to occur to the greatest extent at the points distinguished by asterisks in the systems (VI—X) :*

(IV.)





(V.)

(VI.) $\cdot\overset{*}{\text{C}}\text{H}_2\text{·CMe:CH·CH}_2\cdot$

$\cdot\overset{*}{\text{C}}\text{H}_2\text{·CMe:CH·CH}_2\text{·CH}_2\text{·}\overset{*}{\text{C}}\text{H}_2\text{·CMe:CH·CH}_2\cdot$ (VII.)

$\text{CH}_3\text{·}\overset{*}{\text{C}}\text{H}_2\text{·CH:CH·CH}_3$
(VIII.)

$\overset{*}{\text{C}}\text{H}_3\text{·CMe:CH·CH}_2\text{·CH}_3$
(IX.)

$\text{CH}_3\text{·}\overset{*}{\text{C}}\text{H}_2\text{·CMe:CH·CH}_2\text{·CH}_3$
(X.)

Peroxide Decomposition.—Organic peroxides have very different degrees of stability as is well seen in their widely-varied ease of reduction and their stability at room temperature. It is well attested that the secondary reactions following on the initial formation of peroxide groups commonly involve some loss of unsaturation, and a review of numerous published observations makes it clear that the rapidity of this loss varies with the character (stability or reactivity) of the peroxidic substances formed, and with the experimental conditions. Both of these factors affecting the ease of peroxide decay are very important. In the case of *cyclo*hexene, as seen above, a few hours' autoxidation under the most favourable conditions gives oxygenated material which contains much pure hydroperoxide, but even so the original olefinic unsaturation of the hydrocarbon (per molecule) does not survive in the product wholly undiminished. The same holds good in the case of two other autoxidations which we have studied, *viz.*, those of 1-methyl- and 1 : 2-dimethyl-*cyclo*hexene. If, however, in these examples the temperature during oxidation is allowed to rise above 40°, or the peroxide is formed so slowly (*e.g.*, without catalysis by light or other agency) that the oxidation process is unduly prolonged (*e.g.*, for many days), the yield of pure peroxide becomes much diminished and that of secondary products correspondingly increased. Other substances are similar to *cyclo*hexenes in this respect. Rubber when oxidised rapidly in solution under good illumination at *ca.* 15° incorporates 80% of the oxygen in peroxide form during the early stages of reaction, although later this high yield decreases; but if the oxidation is conducted under less favourable conditions no high percentage of the oxygen intake survives as peroxide at any stage, and in commercial processes, where an organic cobalt salt is used as catalyst and the temperature is allowed to rise unchecked, only traces of peroxide survive. With autoxidised linseed oil many previous observations indicate that the peroxide-content rises during the first few hours to a maximum which represents only a fraction of the total oxygen intake (25—40%, according to the experimental conditions), and afterwards slowly decreases: at the same time the unsaturation decreases.

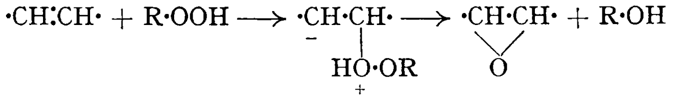
The fact that the increase in the oxygen uptake (with concomitant formation of peroxidic matter) is accompanied by a decrease in the unsaturation of the material has usually been interpreted to mean that oxygen adds directly in peroxide form at the double bonds, although the gross inexactitude of the quantitative relationship between the two has been a continual source of perplexity. Scrutiny of the wealth of recorded data on autoxidative changes leaves little doubt but that the diminution in unsaturation, whether this is slow or rapid, is partly a matter of the experimental conditions. This is understandable if the primary reaction (*i.e.*, the absorption of oxygen to form peroxide groups) is recognised to consist quite generally in the formation of hydroperoxide groups on the α-methylenic carbon atoms, for then the actual oxygen absorption does not affect at all the unsaturation of the system: only later, when the secondary reactions brought into being by the decay of peroxide groups begin, does the unsaturation become affected, and the prevailing conditions of reaction are likely to influence materially the speed of decay and hence the length of life of the peroxide groups and probably to affect the mode of their decomposition. The secondary

---

* This expectation is most completely fulfilled in the analogous attack on the α-methylene groups of olefins by selenium dioxide in the presence of acetic acid. Here, acetoxy-groups become substituted in the following systems at the points marked by asterisks (Guillemonat, *Ann. Chim.*, 1939, **11**, 143): $\overset{*}{\text{C}}\text{H}_3\text{·CMe:CHMe}$, $\text{CH}_3\text{·}\overset{*}{\text{C}}\text{H}_2\text{·CMe:CH}_2$, $\overset{*}{\text{C}}\text{H}_3\text{·CPr}^{\beta}\text{:CHMe}$, $\overset{*}{\text{C}}\text{H}_3\text{·CMe:CHEt}$, $\text{CH}_3\text{·}\overset{*}{\text{C}}\text{H}_2\text{·CPh:CHMe}$, $\text{CH}_3\text{·}\overset{*}{\text{C}}\text{H}_2\text{·CH:CHMe}$, $\overset{*}{\text{C}}\text{H}_2\text{R·CEt:CH·CH}_2\text{R}$, $\text{CHMeR·CH:CH·}\overset{*}{\text{C}}\text{H}_2\text{R}$. The similarity of selenium dioxide oxidation to peroxidation is remarkable.

reactions tend almost entirely towards saturation of the olefinic centres (unless conditions which promote dehydration of the secondary products are employed), and hence the ultimate autoxidation products will often contain but little peroxide and be almost saturated : the actual peroxide content and the condition of unsaturation at intermediate points will depend mainly on the respective rates of formation and decomposition of the peroxide. What these reactions are, and the way in which their course and progress are affected by the experimental conditions, is shown in part below.

As noted by Criegee, the peroxide of *cyclo*hexene which is formed in a few hours under good illumination at about 30° is much purer than Hock's original product, formed during a long period (200 hours) in diffused light. But even the best products, in spite of being distilled expeditiously at pressures below 1 mm. (bath temperature below 80°), give a small peroxide fraction, of rather low peroxide content and slightly high boiling point, in which some degree of secondary change has occurred; any elaborate fractionation of the peroxide unless by molecular distillation at low temperatures serves only to increase this fraction. We have found also that even under the most favourable conditions of operation the oxidation product does not consist of unchanged *cyclo*hexene and the hydroperoxide fraction only. Careful fractionation of the *lower-boiling portion* of the product at reduced pressure always gives some *cyclo*hexene oxide and some *cyclo*hexenol in addition to the unchanged *cyclo*hexene; and if this fractionation is conducted at atmospheric pressure, some of the *cyclo*hexenol is dehydrated, and the water so liberated hydrates a part of the *cyclo*hexene oxide to *trans-cyclo*hexanediol, m. p. 104°. That the oxide and *cyclo*hexenol are formed during the oxidation, and not subsequently, can be demonstrated by reducing the oxidation product with sodium sulphite immediately the oxygen intake ceases, and then fractionating the peroxide-free mixture. It is difficult to envisage any likely means of formation of the simple olefin oxide (*e.g.*, by the hydrolysis or reduction of, or by the loss of free oxygen from, the peroxide) under the conditions of reaction employed other than the direct oxidation of *cyclo*hexene by the *cyclo*hexene peroxide. This would be analogous to the oxidation of olefins to oxido-derivatives by peracids such as perbenzoic acid, and might be represented as being initiated by the occurrence of co-ordination between a polarised ethylenic carbon and a peroxidic oxygen atom, and completed by the elimination of a molecule of alcohol (*cyclo*hexenol) from the co-ordination complex :



$$\cdot\mathrm{CH{:}CH}\cdot + \mathrm{R{\cdot}OOH} \longrightarrow \cdot\underset{-}{\mathrm{CH}}\cdot\underset{\substack{|\\ \underset{+}{\mathrm{HO}}\cdot\mathrm{OR}}}{\mathrm{CH}}\cdot \longrightarrow \cdot\mathrm{CH}\cdot\underset{\substack{\diagdown\diagup\\ \mathrm{O}}}{\mathrm{CH}}\cdot + \mathrm{R{\cdot}OH} \quad . \quad . \quad . \quad . \quad (A)$$

It is important to note that the formation of *cyclo*hexene oxide in this way must necessarily involve a bimolecular reaction, and it was of interest to discover whether, by heating together the suggested reactants, *cyclo*hexene oxide is produced. Tests of this kind carried out at 100° gave *cyclo*hexene oxide in small yield, together with *cyclo*hexenol * and some polymeric material. It is readily understood why no large yield of oxido-compound is formed, since the latter is likely to react at 100° (especially in the presence of small amounts of acid) † with the hydroxylic materials present. The rapid autoxidation of 1-methyl- and of 1 : 2-dimethyl-*cyclo*hexene at 30—40° in ultra-violet light was also found to give rise to the corresponding oxides (1-methyl- and 1 : 2-dimethyl-*cyclo*hexene 1 : 2-epoxide) and alcohols (1-methyl*cyclo*hexenol and 1 : 2-*dimethyl*cyclo*hexen*-3-*ol*), in about equal amounts, as well as to a good yield of the parent *hydroperoxides*; here, however, the low-boiling decomposition products were produced in rather larger yield. The oxides gave on hydrolysis with water at 110°, or better with dilute sulphuric acid, the high-melting forms (respectively) of 1-methyl- and 1 : 2-dimethyl-*cyclo*hexane-1 : 2-diol. The alcohol from the peroxide of 1-methyl*cyclo*hexene proved to be a mixture of the 6- and the 3-hydroxy-compound, the former preponderating, so that the peroxide, in conformity with the views on the point of oxidative attack expressed above, contained both the 6- and the 3-hydroperoxide. This fact received confirmation in several ways.

Ketone Formation.—As seen above, one of the decomposition products of *cyclo*hexene hydroperoxide is *cyclo*hexene-3-ol, and it is a striking fact, noted by Schmidt (*Ber.*, 1930, **63**, 1139), that in various autoxidations of cyclic olefins described in the literature similar unsaturated alcohols have almost invariably been obtained. A review of the examples shows that the hydroxy-group is attached to that one of the ring carbon atoms at which in our view hydroperoxidation would be most likely to occur, except that in the case of α-pinene, in which the system $\cdot CH_2\cdot CH{:}CMe\cdot CH{<}\substack{C\\C}$ occurs, attack at both (alternatively) of the

---

* It is difficult in experiments of this kind to demonstrate with certainty that the *cyclo*hexene oxide and *cyclo*hexenol are formed in molecularly equivalent amounts.

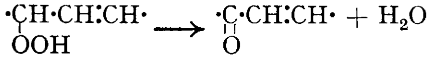
† Some proportion of organic acid formed by chain scission is likely to appear as reaction proceeds, or more rapidly at the temperature of distillation.

α-carbon atoms has been observed. These autoxidations have been carried out at 70° or above, or for long periods at a lower temperature, usually in presence of a catalyst. In many of the examples (*e.g.*, see Table I) the alcohol is accompanied by the corresponding ketone, and it seems at first sight not unlikely (especially in view of the fact that water is almost invariably formed in olefinic autoxidations) that a direct dehydration of the olefinic hydroperoxide to form a ketone may have occurred:

TABLE I.

Olefin.	Catalyst.	Temp.	Time.	Ketone.	Authors.
*cyclo*Hexene	Os (colloidal)	?	22 hours	*cyclo*Hexan-1-ol-2-one	Willstätter and Sonnenfeld [1]
1-Methyl*cyclo*-hexene	None	95°	?	1-Methyl*cyclo*hexen-6-one	Dupont [2]
,,	Fe phthalo-cyanine	70°	72 hours	,,	Cook [3]
1 : 2-Dimethyl-*cyclo*hexene	None	70°	1 week	1 : 2-Dimethyl*cyclo*-hexen-3-one	Dupont [4]
α-Pinene	None (iron vessel)	Room temp.	6 months	Verbenone	Blumann and Zeitschel [5]
,,	Fe phthalo-cyanine	70°	4 days	,,	Cook [3]
,,	Os; sunlight	?	?	,,	Wienhaus and Schumm [6]
β-Pinene	Co resinate	*ca.* 30°	88 hours	Pinocarvone	Schmidt [7]
Limonene	None	Room temp.	2½ months	Carvone	Blumann and Zeitschel [8]
Tetralin	Fe phthalo-cyanine	70°	12 hours	α-Tetralone	Cook [3]

[1] *Ber.*, 1913, **46**, 2952; 1914, **47**, 2814. [2] *Bull. Soc. chim. Belg.*, 1936, **45**, 57. [3] J., 1938, 1778. [4] *Bull. Soc. chim. Belg.*, 1936, **46**, 21. [5] *Ber.*, 1913, **46**, 1178. [6] *Annalen*, 1924, **439**, 20. [7] *Loc. cit.* [8] *Ber.*, 1914, **47**, 2623.



$$\cdot\underset{\substack{|\\ \text{OOH}}}{\text{CH}}\cdot\text{CH:CH}\cdot \longrightarrow \cdot\underset{\substack{\|\\ \text{O}}}{\text{C}}\cdot\text{CH:CH}\cdot + \text{H}_2\text{O} \quad . \; . \; . \; . \; . \; . \; . \; . \qquad (B)$$

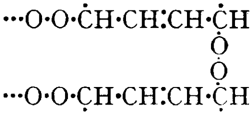
But in none of our autoxidation experiments at 30—40° with *cyclo*hexene or the more rapidly autoxidisable 1-methyl- and 1 : 2-dimethyl-*cyclo*hexene has any recognisable amount of cyclic ketone been formed, although water is a product of reaction. Also, it is plain that to the extent that a hydroperoxide, R·OOH, undergoes dehydration, to that extent it relinquishes its oxidative habit, which much evidence shows to be the principal reactive tendency; furthermore, there is little in the literature to indicate that alkyl peroxides may be able to undergo dehydration, unless the ordinary decomposition of hydrogen peroxide to water and oxygen is accepted as an indication. Nevertheless, both Cook (*loc. cit.*) and Dupont (*Bull. Soc. chim. Belg.*, 1936, **45**, 57) have reported the formation in diffused light at 70° and 90°, respectively, of a cyclic ketone from 1-methyl*cyclo*hexene,* the former author using an active iron catalyst and the latter none at all. It is clear that, whereas the alcohol appears to be a necessary primary decomposition product of the peroxide, the ketone does not; also it appears that for the production of the ketone in appreciable amount either a higher temperature than 40° is required, or some other condition (probably one involving the activity of the catalyst) needs to be fulfilled. We have not succeeded in directly oxidising *cyclo*hexen-3-ol to the corresponding ketone by exposing it to oxygen in ultra-violet light at 30—40°, neither the oxygen nor the organic peroxides which are readily formed from the alcohol under these conditions having apparently the necessary oxidative power. This suggested (although it in no way proved) that the ketone is formed directly from the peroxide, rather than indirectly *via* the alcohol. Hence it seemed most reasonable to look for the origin of the ketone in the isomerising capacity or in one of the paths of direct decomposition of the hydroperoxides.

Ketone Formation by Isomerisation of the Peroxides or Oxides.—The autoxidation of conjugated diolefins appears to yield either polymolecular peroxides in which the diene units are terminally linked as in (XI) (Bodendorff, *Arch. Pharm.*, 1933, **271**, 1) or unimolecular ones such as ascaridol (terpinene peroxide) and the peroxides of 2 : 4-cholestadiene, ergosterol, dehydroergosterol, rubrene, naphthacene, pentacene, anthracene, etc. In all of these unimolecular examples the existing evidence leaves little doubt as to the formation of the peroxides by the transannular addition of oxygen at the ends of conjugated diene systems

---

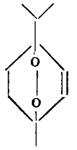
* Cook called the ketone 1-methyl*cyclo*hexen-3-one and the cyclic alcohol 1-methyl*cyclo*hexen-3-ol, whereas Dupont considered his ketone and alcohol to be 1-methyl*cyclo*hexen-6-one and 1-methyl*cyclo*hexen-6-ol respectively. As indicated above, owing to the formation in the original oxidation of two isomeric forms of the hydroperoxide, both the 6- and the 3-alcohol could hardly fail to be present in Cook's and Dupont's preparations; and if the ketone is formed directly from the alcohol or from the parent peroxide, then both the 6- and the 3-ketone would also be present (see below).

(for review of evidence, see Bergmann and McLean, *Chem. Rev.*, 1941, **28**, 367). Now in the case of ascaridol (XII) it has been shown that the transannular peroxide passes on heating at 150° into the oxide (XIII), whilst the peroxide formed from 2 : 4-cholestadiene under mild illumination isomerises (in alcohol solution) on exposure to sunlight to give a saturated ketone. The same ketone is formed directly from the cholestadiene if oxygenation takes place in sunlight, and Skau and Bergmann (*J. Org. Chem.*, 1939, **3**, 66) suggest that the peroxide (XIV) isomerises first to the oxide (XV), which immediately rearranges to give the ketone (XVI); the location of the carbonyl group, however, at position 3 or 4 in (XVI) has not yet been precisely determined. Ergosterol peroxide can also be converted into an epoxide-ketone, but in this case by heating at 185—190° (Windaus, Bergmann, and Luttringhaus, *Annalen*, 1929, **472**, 195; see also Skau and Bergmann, *loc. cit.*); the ketone group has not been shown to appear in the bridged ring, and indeed it may well occur at an original centre of unsaturation in the side chain (Bergmann and McLean, *loc. cit.*, p. 377).

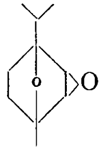


$$\begin{array}{l}\cdots O{\cdot}O{\cdot}\dot{C}H{\cdot}CH{:}CH{\cdot}\dot{C}H\\ \qquad\qquad\qquad\qquad\quad O\\ \qquad\qquad\qquad\qquad\quad O\\ \cdots O{\cdot}O{\cdot}\underset{\cdot}{C}H{\cdot}CH{:}CH{\cdot}\underset{\cdot}{C}H\end{array}$$

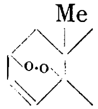
(XI.)



(XII.)

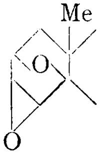


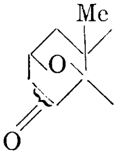
(XIII.)



(XIV.)

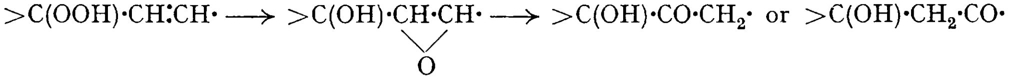
(XV.)



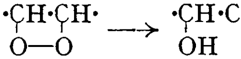


(XVI.)

Amongst recorded investigations of the autoxidation of unconjugated olefinic substances there is, so far as we are aware, no clear instance where direct isomerisation of peroxide to ketone (similar to the foregoing examples in the conjugated series) has been demonstrated. The analogous change in the unconjugated olefin series to that represented by the transformation (XIV) ⟶ (XV) ⟶ (XVI) would be :



$$>C(OOH){\cdot}CH{:}CH{\cdot} \longrightarrow >C(OH){\cdot}\underset{\diagdown\,O\,\diagup}{CH{\cdot}CH}{\cdot} \longrightarrow >C(OH){\cdot}CO{\cdot}CH_2{\cdot} \text{ or } >C(OH){\cdot}CH_2{\cdot}CO{\cdot}$$

Morrell and his collaborators (*loc. cit.*; also *J. Soc. Chem. Ind.*, 1931, **50**, 27T; 1936, **55**, 237T; 1939, **58**, 159T; *J. Oil Colour Chem.*, 1940, **23**, 103) have claimed that enolisable α-ketols are normally formed in the case of autoxidised drying-oil acids or glycerides in the manner:  $\underset{O\text{—}O}{{\cdot}CH{\cdot}CH{\cdot}} \longrightarrow \underset{OH}{{\cdot}CH{\cdot}CO{\cdot}}$, but we can find no justification of the claim in any of the experimental evidence which these authors advance; and indeed, the measurement of ketol content in terms of carbonyl and active hydrogen content by these and other authors (cf. Bolam and Sim, *J. Soc. Chem. Ind.*, 1941, **60**, 507) is necessarily rendered invalid by the fact that the peroxide groups present are highly oxidative, hydroxylic ·OOH groups, and not the less reactive, non-hydroxylic ·O·O· groups assumed by them. In numerous autoxidations of *cyclo*hexene and 1-methyl*cyclo*hexene we have found none of the easily recognisable α-ketol among the oxidation products, although Willstätter and Sonnenfeld (*loc. cit.*), as noted above, obtained some α-ketol (*cyclo*hexan-1-ol-2-one) under their conditions of autoxidation. In view, however, of the frequent formation of α-ketols as intermediates during the oxidative scission of double bonds (*e.g.*, by permanganate) this product seems most likely to have been derived by the further oxidation of the corresponding epoxide or saturated 1 : 2-diol. At present, therefore, the occurrence of a substantial degree of ketone formation by an isomerisation of peroxide groups analogous to that reported for conjugated compounds seems doubtful, but it is hoped to publish further observations on this point later.

Ketone Formation by Peroxide Decomposition.—Various authors have referred to the dual rôle of autoxidation catalysts in promoting both peroxidation and the subsequent decomposition of the peroxides, although the balance between formation and decomposition does not appear to have been studied. Cook (*loc. cit.*) obtained methyl *cyclo*hexenone by autoxidation of methyl*cyclo*hexene at 70°, using ferrous phthalocyanine as catalyst, but in our experiments no significant amount of ketone was formed by oxidation in ultra-violet light at *ca.* 35°. We have therefore tested the ketone-forming action of Cook's catalyst on pure methyl*cyclo*hexene hydroperoxide, and found that this catalyst promotes a very energetic decomposition of the peroxide to cyclic alcohol, cyclic ketone, and other products, the ketone being in substantial yield and consisting of two isomeric compounds, 1-methyl*cyclo*hexen-6- and -3-one. Of these isomerides the former preponderated, so it is fairly certain that they are derived directly from the corresponding alcohols or the parent hydroperoxides. In the case of *cyclo*hexene hydroperoxide ferrous phthalocyanine caused similar energetic decomposition with formation of much *cyclo*hexenol, a substantial yield of ketone, a little *cyclo*pentene-1-aldehyde, and other products. The ketone was *cyclo*hexene-3-one, and the aldehyde a scission product formed by causes discussed later. Similarly, decomposition of 1 : 2-dimethyl*cyclo*hexene hydroperoxide gave a substantial yield of 1 : 2-dimethyl*cyclo*hexen-3-one, together with the related cyclic alcohol and other products. The ketone was contaminated with a little of a second ketone which appeared to be the ring-scission product, 1 : 4-diacetylbutane.

As regards the identity of the immediate precursor of the ketonic products (hydroperoxide or alcohol) in these catalytic decompositions, the evidence is not yet clear. Water is always eliminated in the decompositions, as though by dehydration of the hydroperoxide (equation B), but so it is in autoxidations in which no ketonic product is formed. The normal decomposition product of the peroxide always appears to be the cyclic alcohol, and to permit the formation of this substance the potential oxidising power of the active peroxide groups must be dissipated. This oxidising capacity is largely utilised in oxidative attack, culminating in chain scission, at the unsaturated centres, but it may well be that in the presence of an active catalyst it is sufficiently energetic to bring about the oxidation of the cyclic alcohol to the corresponding ketone. A crucial test on this point remains to be applied. It is of interest, however, to note that the ketones formed in this way by catalytically-promoted peroxide decomposition, unlike those which would be formed by peroxide isomerisation, are unsaturated, whereas the trend of autoxidation in vegetable oils seems, according to published observations, to be towards the production of complete saturation. Possibly the formation of unsaturated ketones is mainly a special characteristic of hydroaromatic autoxidations.

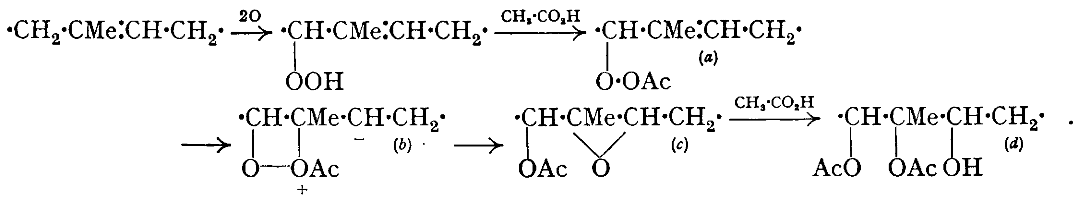
Vigorous decomposition of *cyclo*hexene hydroperoxide occurs when it is heated to about 120° in an open vessel. The reaction is probably similar to that promoted by ferrous phthalocyanine, but the products have not been closely examined.

Oxidative Action of Hydroperoxides in the Presence of Acids.—One of us, with Bloomfield (*J. Soc. Chem. Ind.*, 1935, **54**, 2T), observed that the oxidation of rubber when carried out in presence of a cobalt catalyst is greatly accelerated if a little acetic anhydride is added; moreover, the action of the acetic anhydride is not simply catalytic, since the oxidation products are extensively acetylated. Later, one of us noticed that when small lumps of rubber are refluxed for a day with acetic anhydride, little save slight swelling of the rubber ensues, but when the anhydride is refluxed rapidly over the rubber in an open extraction tube, the hydrocarbon undergoes rapid and advanced degradation in which atmospheric oxidation is the principal factor. The influence of acids does not appear to be confined to organic acids, since attempts to hydrate dihydromyrcene, $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_3$, by refluxing it with sulphuric acid in an open vessel (with a little silver sulphate as hydration catalyst) gave oxidation products instead of hydration products. On the other hand, alkali has no marked promoting action on the autoxidation of rubber, although pyridine appears to assist reaction.

The reactive hydroperoxides which are formed under nearly anhydrous conditions by the action of oxygen on olefins would be expected to react immediately with organic acids to give alphyl esters of the corresponding peracids,

$$R{\cdot}OOH + R'{\cdot}CO_2H \longrightarrow R'{\cdot}C(OH)_2{\cdot}OOR \longrightarrow R'{\cdot}CO{\cdot}OOR + H_2O \quad . \quad . \quad . \quad (C)$$

which in turn would behave like free peracids in their additivity to olefinic centres :

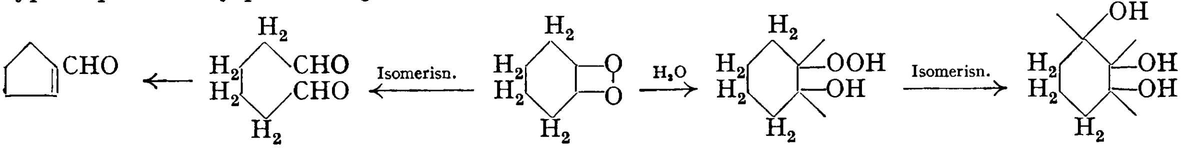


$$\cdot CH_2{\cdot}CMe{:}CH{\cdot}CH_2\cdot \xrightarrow{2O} \underset{\displaystyle OOH}{\cdot CH}{\cdot}CMe{:}CH{\cdot}CH_2\cdot \xrightarrow{CH_3{\cdot}CO_2H} \underset{\displaystyle O{\cdot}OAc}{\cdot CH}{\cdot}CMe{:}CH{\cdot}CH_2\cdot \ (a)$$

$$\longrightarrow \underset{\displaystyle O}{\cdot CH}{\cdot}\underset{\displaystyle \overset{—}{}OAc^{+}}{CMe}{\cdot}\overset{-}{CH}{\cdot}CH_2\cdot \ (b) \longrightarrow \underset{\displaystyle OAc}{\cdot CH}{\cdot}CMe{\cdot}CH{\cdot}CH_2\cdot\ (\text{CMe–O–CH}) \ (c) \xrightarrow{CH_3{\cdot}CO_2H} \underset{\displaystyle AcO}{\cdot CH}{\cdot}\underset{\displaystyle OAc}{CMe}{\cdot}\underset{\displaystyle OH}{CH}{\cdot}CH_2\cdot \ (d) \quad . \quad . \quad (D)$$

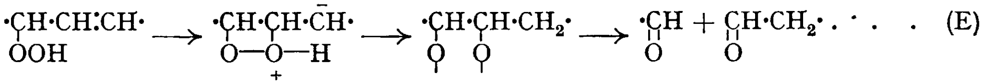
The epoxide shown in stage (*c*) probably never appears as an isolable compound; also the addition of acetic acid at the epoxy-group (change *c* ⟶ *d*), and of •OAc at the double bond (change *a* ⟶ *b*), may take place in the reverse direction to that shown in scheme (D). The reaction in presence of an acid anhydride would be precisely analogous, yielding eventually for pure acetic anhydride (free from acetic acid) triacetoxy-derivatives, $\cdot CH(OAc){\cdot}CMe(OAc){\cdot}CH(OAc){\cdot}CH_2\cdot$; but with either the free fatty acid or the anhydride further oxidative attack might lead to scission between either pair of oxygenated carbon atoms, although this probably would not occur nearly so readily with esterified polyalcohols as with the corresponding free alcohols. The satisfactory confirmation of such a course of reaction in the case of rubber has only recently become possible by the development in connexion with this work of a precision method for the determination of active hydrogen in high-molecular substances (Bolland, *Trans. Inst. Rubber Ind.*, 1941, **16**, 267). The details of this confirmation form the subject of Part III.

Whether or no in the above-cited oxidation of dihydromyrcene in presence of dilute sulphuric acid there is slow and transient formation of peracid (? permonosulphuric acid), there is certainly engendered a vigorous peroxidic oxidising capacity when pure *cyclo*hexene- and alkyl*cyclo*hexene-hydroperoxides are mixed with dilute sulphuric acid. Hock (*Oel u. Kohle, loc. cit.*) observed that *cyclo*hexene peroxide, when allowed to stand with sulphuric acid at 35—40°, gave mainly *cyclo*pentenealdehyde (*ca.* 20% yield) and *cyclo*hexane-1 : 2 : 3-triol (50% yield),* and he sought to explain their formation from a supposed cyclic type of peroxide by postulating two isomerisations :



Now the triol is precisely the product which would be expected to arise in accordance with the foregoing schemes (C) and (D) if an aqueous mineral acid were substituted for the organic acid or anhydride, but the formation of *cyclo*pentenealdehyde (*i.e.*, the dehydrated aldol from adipic dialdehyde) is more difficult to formulate, since the oxygeno-substituent has apparently disappeared from the α-carbon atom. It seemed possible at first that the parent adipic dialdehyde might have arisen by the action of the hydroperoxide, and subsequently perhaps of peracid, on residual *cyclo*hexene in the peroxide employed (Equation A), but many repetitions of Hock's experiment with peroxide which had been entirely freed from *cyclo*hexene have always given some *cyclo*pentenealdehyde together with a little *cyclo*hexenol, although the main products were *cyclo*hexanetriol and a " dimeric " acidic residue; moreover, we have found that by heating the peroxide with water at 110° the same four products are formed but in different proportions. Hence, in order to account for the formation of *cyclo*pentenealdehyde, it is necessary either to envisage a reaction, inter- or intra-molecular in kind, in which the peroxide group acts oxidatively at the double bond and simultaneously disappears entirely from the α-methylene group, or alternatively to look for the source of the *cyclo*pentenealdehyde in the incomplete homogeneity of the hydroperoxide used.

Now it is uncertain whether the changes expressed in equations (A) and (D), or indeed the peroxide→oxide→ketone-conversion of the above-mentioned trans-annular peroxides, are necessarily always intramolecular ones, but the transformation of pure *cyclo*hexene hydroperoxide into adipic dialdehyde by the action of dilute sulphuric acid must necessarily be intramolecular, since otherwise the formation of α-hydroxyadipic dialdehyde would be inescapable. A conceivable course of reaction is the following, in which co-ordination of an ethylenic carbon atom with a peroxidic oxygen atom gives an oxonium complex, which on disruption produces momentarily a di-radical, and ultimately (by scission) two aldehyde groups :


$$\underset{\text{OOH}}{\cdot\text{CH}}\cdot\text{CH}\!:\!\text{CH}\cdot \longrightarrow \underset{\text{O}}{\cdot\text{CH}}\cdot\underset{\overset{-}{\underset{+}{\text{O}}}\text{—H}}{\text{CH}}\cdot\text{CH}\cdot \longrightarrow \underset{\text{O}}{\cdot\text{CH}}\cdot\underset{\text{O}}{\text{CH}}\cdot\text{CH}_2\cdot \longrightarrow \underset{\text{O}}{\overset{}{\cdot\text{CH}}} + \underset{\text{O}}{\text{CH}}\cdot\text{CH}_2\cdot \quad . \quad . \quad . \qquad \text{(E)}$$

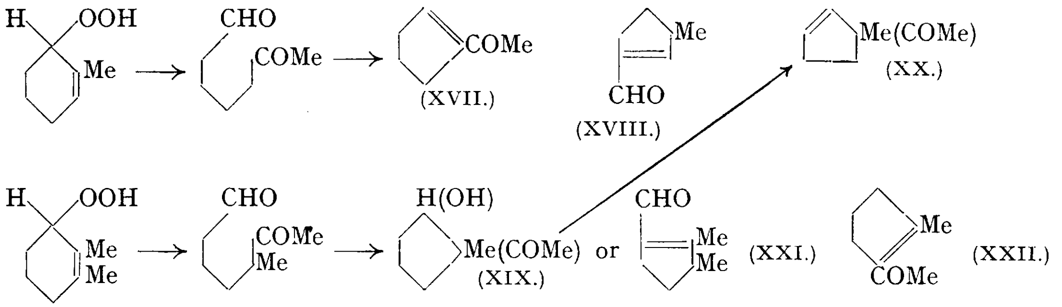
By this mechanism scission of the *cyclo*hexene could occur without loss of any carbon atoms at a single bond adjacent to the original double bond, and adipic dialdehyde could thus be formed. But if this course of reaction were correct, 1-methyl*cyclo*hexene 6-hydroperoxide would be expected to give with sulphuric acid 1-acetyl*cyclo*pentene (XVII), and the isomeric 3-hydroperoxide similarly to give the aldehyde (XVIII). Likewise 1 : 2-dimethyl*cyclo*hexene 3-hydroperoxide should give either 1-acetyl-1-methyl*cyclo*penten-2-ol (XIX) [leading possibly to its dehydration product 1-acetyl-1-methyl*cyclo*pentene (XX)] or 2 : 3-dimethyl*cyclo*penten-1-aldehyde (XXI).

We have found that the normally-formed mixture of 1-methyl*cyclo*hexene 6- and 3-hydroperoxides does indeed give 1-acetyl*cyclo*pentene (nearly 5% yield), together with 1-methyl*cyclo*hexanetriol (40—50% yield) and a little methyl*cyclo*hexenol, but no aldehyde or second carbonyl compound is formed; also 1 : 2-dimethyl*cyclo*hexene 3-hydroperoxide gives quite analogously a mixture of a ketone, $C_8H_{12}O$, much 1 : 2-*dimethyl*cyclo*hexane-*?1 : 2 : 3-*triol*, and a little 1 : 2-dimethyl*cyclo*hexen-3-ol. The ketone $C_8H_{12}O$, however, is found to be, not (XX), but the well-known acetylmethyl*cyclo*pentene (XXII) which would

---

* In his first communication Hock (*Naturwiss.*, 1936, **24**, 159) announced the formation of a 50% yield of *cyclo*hexane-1 : 2-diol, m. p. 104°, but subsequently claimed high yields of the triol. In our repetitions of Hock's experiments we have always obtained the triol, but never the diol.

result *via* 1 : 4-diacetylbutane from fission of the *cyclo*hexene ring at the double bond; moreover, the crude ketone contains a little 1 : 4-diacetylbutane. The formation of only the one observed cyclic carbonyl compound from the isomeric hydroperoxides of 1-methyl*cyclo*hexene, and that of the ketone (XXII) from the hydroperoxide of 1 : 2-dimethyl*cyclo*hexene, shows quite clearly that primary fission of the *cyclo*hexene ring occurs only at the original double bond. It must be concluded, therefore, that the formation of *cyclo*pentenealdehyde, of acetyl*cyclo*pentene, and of acetylmethyl*cyclo*pentene from the hydroperoxides of *cyclo*hexene, methyl*cyclo*hexene, and dimethyl*cyclo*hexene, respectively, is due to the presence of some secondary oxidation product in even the best specimens of hydroperoxide obtained.



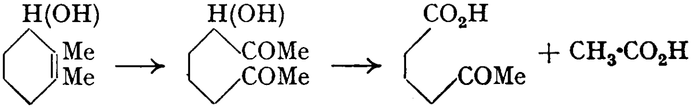
(XVII.) (XVIII.) (XX.) (XIX.) (XXI.) (XXII.)

Special tests with *cyclo*hexene hydroperoxide and methyl*cyclo*hexene hydroperoxide showed that the proportion of *cyclo*pentenealdehyde or acetyl*cyclo*pentene formed increased very markedly (up to 10% yield) when slightly high-boiling specimens of hydroperoxide of more or less low peroxidic oxygen content were treated with sulphuric acid; but no single specimen of hydroperoxide prepared by our usual procedure (rapid oxidation of the hydrocarbon followed by two distillations with the distillation-bath below 80°), even although it showed a correct peroxidic oxygen content, gave a sulphuric acid reaction product which was entirely free from the by-products in question. The discrepancy concerning the peroxide content is easily explicable, since the best method of determination available (see p. 133) is liable to an error of ± 5% of the true value; it seems clear, therefore, that some more rigorous procedure than the one adopted would be necessary in order to prepare the hydroperoxides entirely free from their secondary decomposition products.

The impurity is probably the saturated diol derived from *cyclo*hexene *via* the epoxide (equation A), and indeed, very small yields of this substance have been isolated on several occasions from the " dimeric " residue left after distillation of the peroxide (see below).

Oxidative Action of Hydroperoxides in the Presence of Alkali.—Hock and Gänicke (*Ber.*, 1938, **71**, 1430) found that when *cyclo*hexene peroxide is shaken with dilute sodium hydroxide solution at a temperature not above 30°, much *cyclo*hexenol is formed, together with a mixture of acids comprising α-hydroxyadipic and adipic acids, as well as small amounts of glutaric acid and volatile fatty acids which are doubtless formed by further oxidation of hydroxyadipic acid. *cyclo*Hexen-6-ol is the normal hydrolysis product of the hydroperoxide ($R\cdot OOH + H\cdot OH \longrightarrow R\cdot OH + H_2O_2$) and we have obtained yields of this alcohol up to 80% of the theoretical. α-Hydroxyadipic acid, formed by the oxidative action of liberated hydrogen peroxide (or possibly to some extent of *cyclo*hexene hydroperoxide) on *cyclo*hexenol or *cyclo*hexene hydroperoxide, is also to be expected, and Hock has shown that this is the principal acidic product (40% of total acids; overall yield, 7·8%). The formation, however, of adipic acid (9% of the total acids in Hock's experiments; overall yield, 1·9%), which we have qualitatively verified, requires explanation, since if the acid is formed from *cyclo*hexene 6-hydroperoxide the α-carbon atom must in this case also have become in some unusual way deoxygenated. We have no doubt that the source of the acid, like that of the *cyclo*pentenealdehyde formed by the action of water, sulphuric acid, heat, or a decomposition catalyst (see below) on the peroxide, is the same non-peroxidic impurity contained in the peroxide used which was referred to above. The 1 : 2-diol would be likely to undergo ready attack by hydrogen peroxide or alkyl hydroperoxide in alkaline solution.

1 : 2-Dimethyl*cyclo*hexene 3-hydroperoxide gave with alkali much 1 : 2-dimethyl*cyclo*hexen-3-ol, together with the expected oxidation products, γ-acetylbutyric and acetic acids. There was formed also in very small yield a high-melting, water-soluble acid (m. p. 196—197°).



1-Methyl*cyclo*hexene hydroperoxide gave analogously much methyl*cyclo*hexenol and a mixture of several other products, including (*a*) a little γ-acetylbutyric acid derived from the 3-substituted component of the hydroperoxide mixture, (*b*) a high-melting, water-soluble *acid*, $C_7H_{10}O_2$ (m. p. 207°) very similar to the one from dimethyl*cyclo*hexene hydroperoxide, which remained unreduced on treatment with hydrogen and platinum but was readily oxidised by permanganate to a highly oxygenated acid (? $C_7H_{10}O_6$) of m. p. 69°, and (*c*) a syrupy mixture of acids doubtless containing the oxidative scission products of the 6-hydroperoxide. The high-melting acid, $C_7H_{10}O_2$, was not certainly identified but probably retained the *cyclo*hexane ring intact. Much of the oxidative action promoted by the action of alkali is probably due to the hydrogen peroxide formed by hydrolysis of the hydroperoxides.

Formation of Dimeric Products.—Stephens (*loc. cit.*) reported that when *cyclo*hexene peroxide was isolated by fractional distillation there remained behind a considerable liquid residue which, from its empirical composition and molecular weight, he concluded to be a dimeride of the peroxide containing one peroxide group and probably one active hydrogen atom (Found : 0·68 atom) per molecule. We have analysed a number of these residues from *cyclo*hexene and methyl*cyclo*hexene hydroperoxides, and found them to have approximately the characteristics described by Stephens. The amounts of residues formed in our experiments depended largely on the duration of heating during fractionation, or of exposure to ultra-violet light during the oxidation. New quantities of high-boiling residue were certainly formed at each distillation of the peroxide, but a good deal of the residue ordinarily isolated from oxidation products seemed to be formed during the original oxidation. Irradiation of the isolated hydroperoxide in a nitrogen atmosphere gave viscous yellow polymeric residues.

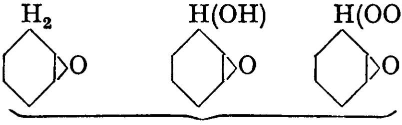
Now, the intermolecular additions which occur during the autoxidation of these simple unsaturated hydrocarbons are widely encountered in the autoxidation of other olefinic substances and are specially important in the case of the drying oils (and apparently of rubber) where oxygenated gels and insoluble materials of high molecular weight are ultimately produced. Hence the elucidation of the mechanism of reaction in the simple examples is of considerable interest. This kind of polymerisation has been suspected to be a function of peroxidation or of peroxide breakdown (or both), but has not been clearly differentiated from the purely olefinic additions (involving carbon-to-carbon intermolecular linking) which constitute the ordinary thermal polymerisation reactions of unconjugated olefins, although much evidence shows that the thermal polymerisations require for their promotion temperatures well above 200°, whereas the autoxidation polymerisations can take place at ordinary or only moderately elevated temperatures.

A preliminary examination of many " dimeric " residues from the hydroperoxides of *cyclo*hexene and methyl*cyclo*hexene has shown that these materials are highly heterogeneous, even although their average composition and molecular weight correspond closely with those required by the strict dimeric formula. This is seen if the residues are extracted with water and with dilute alkali, when usually three types of material, *viz.*, (i) neutral water-insoluble, (ii) neutral water-soluble, and (iii) acidic water-soluble, are obtainable. None of these fractions is entirely homogeneous, as distillation (with or without preliminary reduction of peroxide groups) shows, and hence the dimeride of even so simple a hydroperoxide as that of *cyclo*hexene must be recognised to contain a considerable range of individuals, formed either by interaction of different products in the autoxidation mixture or else by oxidative modification (with perhaps some dehydration) of the first-formed dimeric products.

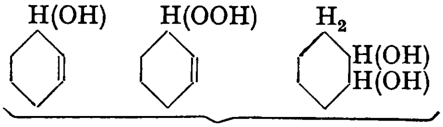
The peroxide content of the residues has been found to depend considerably on the treatment, and especially the thermal treatment, they have received during their formation and isolation. It falls considerably (even as low as *ca.* 3%) when the original oxidation process or the subsequent distillation procedure is unduly prolonged or carried out at an unusually high temperature. Indeed, it is clear that heating at 70—100° causes fairly rapid progressive decomposition of the peroxide groups present (including those of unremoved monomeric hydroperoxide) with concomitant oxidative attack at the double bonds and rapid increase in the complexity of the system. Isolation of individual dimeric products by fractional distillation is thus well-nigh impossible, and even if all peroxide groups in an original oxidation product are reduced before any distillation is begun, the polymeric residue ultimately obtained is still heterogeneous.

A large proportion of the neutral, water-insoluble fraction obtained from the polymeric residues has a composition, when freed from residual peroxide groups by reduction, between $C_{12}H_{20}O_2$ and $C_{12}H_{18}O$ (as though a mixture of $C_{12}H_{20}O_2$ and its dehydration product), and is almost wholly non-saponifiable. The main bulk of the neutral, water-soluble material approximates in composition to $C_{12}H_{20}O_3$, and is hydroxylic and hygroscopic. The water-soluble acid fraction is hygroscopic and composed mainly of dimeric molecules of approximate average composition between $C_{12}H_{20}O_5$ and $C_{12}H_{20}O_6$ in which one of the six-carbon rings has apparently undergone oxidative scission, although small quantities of monomeric acidic material (chiefly adipic acid) have been isolated by distillation.

The basis of coupling of molecules appears to us probably to reside largely in the interaction of oxido-groups * in one reactant molecule (F) with hydroxylic groups in the other (G), and amongst the possible reactants derived from *cyclo*hexene in the two categories (F) and (G) are :

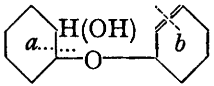


(F.)

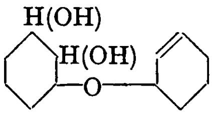


(G.)

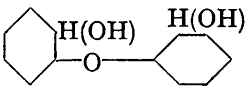
which may give rise to " dimeric " structures such as (XXIII)—(XXV) :



(XXIII.)

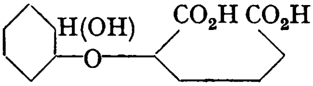


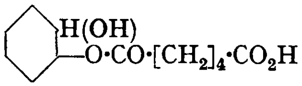
(XXIV.)



(XXV.)

(XXVI.)





(XXVII.)

any of which may undergo some degree of dehydration, oxidative scission (*e.g.*, at *a* or *b* in XXIII), or oxidative hydroxylation (*e.g.*, at *b* in XXIII). Whether peroxido-links formed by interaction of oxido-groups and hydroperoxido-groups ($RO{>}R'{\cdot}O{\cdot}O{\cdot}H \longrightarrow OH{\cdot}R{\cdot}O{\cdot}O{\cdot}R'$) are produced at all is uncertain, but hydrogenation experiments indicate clearly that no considerable part of the dimeric product consists of dicyclyl peroxides (reducible to cyclic alcohols). So far as present experiments show, the bulk of the acidic dimeride is unsaponifiable, and is therefore to be regarded as composed of further-oxidised dimeride molecules such as (XXVI), rather than of dimeride molecules formed by interaction of an oxido-compound and a dibasic acid (*e.g.*, XXVII). The absence of any very large proportion of saponifiable material is probably to be expected in the autoxidation of a neutral olefin, since the production of free carboxylic acid by oxidative chain scission comes at a late stage in the autoxidation process, but such absence may well not hold in the case of the autoxidation of an unsaturated acid, where from the outset of reaction a large concentration of carboxyl groups is available. Indeed, Deatherage and Mattill (*Ind. Eng. Chem.*, 1939, **31**, 1425) have already observed that some considerable part of the autoxidation product of oleic acid is a saponifiable ester, yielding as the alcoholic component 9 : 10-dihydroxystearic acid, thus indicating that interaction between oxidostearic acid and the carboxyl group of oleic or oxygenated oleic acid has occurred. The constitution of oleic acid peroxide is described in Part IV.

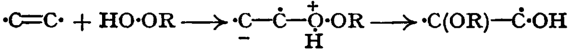
There is, however, another likely mechanism of autoxidation polymerisation, which may play a more or less important part in the secondary changes (thermally or photochemically promoted) which destroy the first-formed hydroperoxide groups. In view of the ready thermal dissociation of dibenzoyl peroxide in liquid media to give free radicals, for which evidence is now strong, it seems probable that free-radical formation ($R{\cdot}OOH \longrightarrow RO{-} + {-}OH$) enters into the normal decomposition of hydroperoxides, giving analogous results to those encountered with other decomposing systems (cf. Hey and Waters, *Chem. Rev.*, 1937, **21**, 169), and especially giving alcohols and ether-like dimerides ($RO{-} + RH \longrightarrow ROH + R{-}$ and $R{\cdot}O{\cdot}R + H{-}$). The course of attack on *cyclo*hexene of the free radicals derived from dibenzoyl peroxide will be described later.

EXPERIMENTAL.

cyclo*Hexene Hydroperoxide*.—Carefully purified *cyclo*hexene, b. p. 83°, contained in a quartz flask connected with an oxygen reservoir, was warmed initially to 35°, shaken continuously, and irradiated by means of a

---

* It may not always be necessary for a hydroperoxide molecule first to decompose to the corresponding oxido-compound before it unites with another molecule. A direct route can be simply formulated whereby one of the reacting molecules requires as functional group a double bond (*e.g.*, an olefin, an olefin hydroperoxide, or an unsaturated alcohol) and the other a hydroperoxide group, thus :



$$\cdot C{=}C\cdot + HO{\cdot}OR \longrightarrow \cdot\dot{C}{-}\underset{-}{\dot{C}}{-}\underset{H}{\overset{+}{O}}{\cdot}OR \longrightarrow \cdot C(OR){-}\dot{C}{\cdot}OH$$

An ether type of dimeride of somewhat variable constitution would still be formed.

Since any hydroperoxide molecule formed in the reaction mixture is normally surrounded by many olefin molecules and fewer hydroperoxide molecules (or their decomposition products), many " dimeric " molecules of type (XXIII) might well be produced.

mercury vapour lamp. For this purpose the flask, containing 100-g. or 200-g. portions of hydrocarbon, was mounted in a mechanical shaker above a small heating bulb, and placed about 6 inches from the lamp. The temperature in the flask usually remained between 35° and 40° without further external heating. The oxygen used was from a cylinder, and was roughly dried by passing through a calcium chloride tube placed between the reservoir and the reaction flask. No special precautions were taken to absorb small quantities of carbon dioxide produced in the oxidation. Usually, absorption of gas began immediately after the shaking and illumination were started, and proceeded at about 1,500 c.c. per hour. The purest peroxide was obtained by rapid absorption of oxygen over a comparatively brief period (3—4 hours), since prolonged exposure to ultra-violet light with the object of converting a larger portion of the hydrocarbon into peroxide produced large yields of a high-boiling alteration product, the so-called " dimer " of Stephens. Too slow absorption of oxygen over a long period, arising from feeble illumination (*e.g.*, diffused daylight or light from an ordinary electric bulb) or from a too low reaction temperature, invariably gave very impure peroxide (containing both low-boiling and high-boiling impurities) owing to the occurrence of secondary peroxidic transformation. In the earlier experiments the low-boiling impurities escaped notice owing to their high volatility and consequent inclusion with the recovered *cyclo*hexene. For the purpose of studying the secondary products a few oxidations were conducted more slowly, usually with feebler illumination.

The reaction mixture *always* contained (*a*) crude unchanged *cyclo*hexene, (*b*) a fraction of b. p. *ca.* 30°/0·2 mm., (*c*) the peroxide, and (*d*) some high-boiling material. These portions were isolated by a preliminary fractionation at 0·5 mm. pressure and then were examined separately. The peroxide fraction could be stored without any serious deterioration in a refrigerator; specimens of high peroxide content were often found to be little changed after storage for many weeks.

Fraction (b), *b. p.* 30°/0·2 *mm.*—Redistillation through a Dufton column gave a slightly syrupy, oxygenated liquid, b. p. 29—30°/0·2 mm., having P.O.C.* 3% (Found : C, 72·35; H, 10·3; iod. val., 198·0. Calc. for $C_6H_{10}O$: C, 73·4; H, 10·3%; iod. val., 259·2) and consisting largely of *cyclo*hexen-3-ol (α-naphthylurethane, m. p. 156°. Found : C, 76·1; H, 6·25; N, 5·35. Calc. for $C_{17}H_{17}O_2N$: C, 76·35; H, 6·4; N, 5·25%) together with a little *cyclo*hexene peroxide. The impure *cyclo*hexanol, after being shaken for a few minutes with 30% aqueous sodium sulphite to reduce *cyclo*hexene peroxide to *cyclo*hexenol, was then peroxide-free, but although it had the empirical formula $C_6H_{10}O$ (Found : C, 73·2; H, 10·2%) it still had only 78·3% of the required unsaturation and less than 80% of the required active hydrogen content (Found : iod. val., 207·5; active H, 0·82. Calc. for $C_6H_9{\cdot}OH$: iod. val., 259·2; active H, 1·03%). The volatile, saturated, oxygenated impurity was the isomeride of *cyclo*hexenol, epoxy*cyclo*hexane.

The combined (*b*) fractions (10·1 g.) from two further portions of *cyclo*hexene which had been oxidised slowly under feebler illumination than usual were refractionated, a Dufton column being used. The major part boiled at 29—30°/0·2 mm. and again consisted of a similar mixture of *cyclo*hexenol, epoxy*cyclo*hexane, and a little peroxide (P.O.C. 2·9%; iod. val., 214·2). The epoxy*cyclo*hexane, owing to its high reactivity when heated, and especially its ready oxidisability, could best be isolated when the crude oxidation product was immediately reduced with sodium sulphite before fractionation was carried out (see below).

When 2 g. of fraction (*b*) which had been freed from peroxide by sodium sulphite were heated with 15 c.c. of water for 4 hours at 115° in a sealed tube in order to hydrolyse the epoxide, *cyclo*hexen-3-ol and a crude water-insoluble " dimeric " *oil*, b. p. 112°/0·2 mm. (Found : C, 75·6; H, 10·0; iod. val., 180·0. $C_{12}H_{20}O_2$ requires C, 73·4; H, 10·3%) were obtained. When a further 2-g. portion of peroxide-free fraction (*b*) was hydrolysed by warming with 20 c.c. of N-sulphuric acid for 48 hours at 40—45°, *cyclo*hexenol together with a similar " dimeric " oil (Found : C, 78·35; H, 10·2%; iod. val., 213·5) were obtained. Several repetitions of these hydrolyses using (*b*) fractions isolated from other oxidation products always failed to give more than very small yields of *cyclo*hexane-1 : 2-diol, showing that the epoxide was destroyed by either procedure, and apparently underwent reaction with *cyclo*hexanol to give the " dimeric " oil. The formation of epoxy*cyclo*hexane was more easily demonstrated by examination of fraction (*a*).

Fraction (c).—Rapid oxidation of *cyclo*hexene during 4 hours usually gave a product from which were obtained on first fractionation a peroxide fraction of P.O.C. 20—25%, and on second fractionation a 15—20% yield (based on the hydrocarbon taken) of substantially pure *cyclo*hexene 3-hydroperoxide, b. p. 47—48°/0·2 mm. (Found : C, 63·25; H, 8·85; P.O.C., 28·0. Calc. for $C_6H_{10}O_2$: C, 63·1; H, 8·85%; P.O.C., 28·05%), together with a little less pure (mostly rather low-boiling) peroxide. The unsaturation of the peroxide was conveniently determined by iodine value, but was always a little low (*ca.* $\lvert\overline{\overline{\;\;\;}}_{0\cdot94}$), owing in part to the occurrence of subsidiary reaction between the peroxide and the potassium iodide reagent. On hydrogenation (Adams's catalyst) the peroxide absorbed 2 mols. of hydrogen, giving, in nearly quantitative yield, immediately crystallisable *cyclo*hexanol [3 : 5-dinitrobenzoate, m. p. 110°, mixed m. p. 110° (Found : C, 53·3; H, 4·75; N, 9·60. Calc. for $C_{13}H_{14}O_6N_2$: C, 53·05; H, 4·8; N, 9·5%); α-naphthylamine complex with the dinitrobenzoate, m. p. 126°, mixed m. p. 126° (Found : C, 62·8; H, 5·1; N, 10·05. Calc. for $C_{23}H_{23}O_6N_3$: C, 63·15; H, 5·3; N, 9·6%)]. The

---

* The peroxidic oxygen content is referred to as P.O.C. and denotes the percentage of oxygen per mol. which is contained in ·(OOH) groups, *i.e.*, twice the percentage of active oxygen per mol. A rapid and convenient method of P.O.C. determination has been devised for use in these investigations by Bolland, Sundralingam, Sutton, and Tristram (*Trans. Inst. Rubber Ind.*, 1941, **16**, 29).

rather low-boiling fractions of peroxide showed a low P.O.C. and absorbed only about 1 mol. (usually 0·95—0·98 mol.) of hydrogen; the hydrogenation product gave, after removal of a small volatile forerun, homogeneous *cyclo*hexanol. This confirmed that the principal normal decomposition product of *cyclo*hexene peroxide is *cyclo*hexenol; and since in slow oxidations the yield of pure peroxide was diminished and that of the low-boiling fractions increased, the conditions for slow oxidation promoted considerable decomposition.

For the efficient reduction of considerable quantities of the peroxide to *cyclo*hexenol, the former was shaken with well-cooled 30% aqueous sodium sulphite solution, at first cautiously to avoid undue heat development, and later for 2—3 hours on a mechanical shaker. The alcohol, when extracted with ether and rectified, boiled at 65—66°/13 mm.

Fraction (a), *b. p.* 60°/100 *mm.*—To avoid the formation of additional by-products or the destruction of the original ones through being heated with peroxide during fractional distillation, the reaction product from 100 g. of hydrocarbon (5 hours oxidation; weight increase, 9·0 g.) was reduced immediately with 30% aqueous sodium sulphite, the reduced product extracted with ether, dried, and freed first from solvent, and then (at slightly reduced pressure) from *cyclo*hexene. The peroxide-free oxidation product gave on fractionation at reduced pressures under a short column the fractions: (i) b. p. below 60°/13 mm. (5·0 g.), (ii) b. p. 64—65°/12 mm. (13·1 g.), (iii) b. p. 80—86°/1 mm. (2·1 g.), (iv) b. p. 94—95°/1 mm. (0·3 g.), and a residue (*ca.* 1 g.). Of these (ii) was almost pure *cyclo*hexenol of nearly correct unsaturation and analytical composition (α-naphthylurethane, m. p. 156°; mixed m. p. 156°), (i) was a mixture of this with much epoxy*cyclo*hexane, and the higher fractions consisted of heterogeneous "dimeric" materials. The epoxide fraction gave a good yield of *trans*-*cyclo*hexane-1 : 2-diol, m. p. 104°, mixed m. p. 104°, on hydrolysis at 40—45° with N-sulphuric acid, and the largest "dimeric" fraction had (assuming homogeneity) an empirical composition approximating to $C_6H_{10}O$ (Found: 77·7; H, 10·2; iod. val., 130·8. Calc. for $C_6H_{10}O$: C, 73·4; H, 10·3%). Repetition of the experiment with 100 g. of *cyclo*hexene gave precisely comparable results, the yield of epoxide being substantial and the fraction (iii) now giving: C, 75·2; H, 10·1%; iod. val., 140.

An attempt to fractionate a further 10 g. of the epoxide fraction at atmospheric pressure caused considerable interaction of the component materials as well as dehydration, with formation of (i) a small quantity of highly unsaturated hydrocarbon, apparently *cyclo*hexadiene, (ii) *cyclo*hexane-1 : 2-diol, m. p. 104° (Found: C, 62·0; H, 10·4. Calc. for $C_6H_{12}O_2$: C, 62·0; H, 10·4%), and a viscous residual liquid. A tolerably pure epoxide fraction, of b. p. 110—120°, convertible into *cyclo*hexanediol, was, however, obtained.

Action of Heat on the Hydroperoxide.—When *cyclo*hexene hydroperoxide was heated, its peroxidic character diminished. The change was relatively slow at room temperature in diffused daylight, but much more rapid when the peroxide was distilled from a bath at 70—80°. A peroxide fraction (16·5 g.) which, when separated from the crude oxidation product by one distillation at 0·5 mm. pressure, had P.O.C. 24·2%, gave on redistillation at the same pressure the fractions (i) b. p. 30—35°, P.O.C. 2—3% (1·8 g.); (ii) b. p. 44—45°, P.O.C. 20·1% (10 g.); (iii) b. p. 45—46°, P.O.C. 28·5% (3·6 g.); and a high-boiling residue (0·8 g.). The chief low-boiling product was *cyclo*hexen-3-ol, but no epoxy*cyclo*hexane was identified. The high-boiling residue approximated in composition to the formula $C_6H_{10}O_2$ (Found: C, 63·75; H, 9·05. Calc. for $C_6H_{10}O_2$: C, 63·1; H, 8·85%) and had P.O.C. 14·3%: it thus corresponded with Stephens's "dimeride."

Action of Ultra-violet Light on the Hydroperoxide.—Peroxide of P.O.C. 27·8% (4. g.) was placed in a quartz flask and the air carefully displaced by oxygen-free nitrogen. The flask was shaken and simultaneously illuminated by ultra-violet light at about 35° for 6 hours. The viscosity of the peroxide increased, its colour changed to light yellow, and its P.O.C. fell by about half to 14·5%; its empirical composition, however, was little or not at all changed (Found: C, 63·8; H, 9·0%). A portion (2·8 g.) of the irradiated material was immediately hydrogenated in alcohol (Adams's catalyst). It absorbed 559 c.c. at N.T.P., *i.e.*, half of that required (1090·4 c.c.) for reducing one double bond and the ·OOH group in C_6H_9·OOH. In view of the observed overall fall of one half of the total P.O.C., due to irradiation, the overall olefinic unsaturation must likewise have diminished by one-half (282 c.c. of hydrogen at N.T.P. used for reducing peroxide, 277 c.c. for reducing double bond). Thus an overall loss by decomposition of one hydroperoxide group was accompanied by the saturation of one double bond. The product, when freed from alcohol, had P.O.C. $< 0.02\%$; it gave on distillation (i) 1·1 g. of *cyclo*hexanol, b. p. 63—64°/14 mm. (ii) 0·6 g. of "dimeric" material, b. p. 110—176°/0·5 mm., and (iii) 0·4 g. of undistilled residue.

3·2 G. of peroxide of P.O.C. 27·8% (Found: C, 63·2; H, 9·0%) were irradiated for 6 hours at *ca.* 35° as above, but in an atmosphere of oxygen. Some oxygen was absorbed (150 c.c.) and the pale yellow liquid product then had P.O.C. 14·35% [Found: C, 58·75; H, 8·2; O (by diff.), 33·05%]. On hydrogenation the product (2·6 g.) absorbed 403 c.c. (average of 0·64 mol.) of hydrogen at N.T.P., so during the irradiation both absorption of oxygen and some saturation of the double bond had occurred. The product consisted of a little *cyclo*hexenol (0·6 g.) and "dimeric" material of b. p. 120°/0·5 mm. and above.

Action of the Hydroperoxide on cyclo*Hexene.*—When equimolecular amounts of the peroxide (3·9 g.) and pure hydrocarbon (2·8 g.) were exposed in a flask to diffused daylight for 4 weeks at room temperature, and the product subsequently hydrogenated, it was found to have undergone no serious reduction of unsaturation (H_2 absorbed, 2250 c.c. at N.T.P.; theory, 2295 c.c.). When a similar mixture (3 g. of each component) was heated for 5 hours on a water-bath, the product was found on fractionation to consist of crude *cyclo*hexene

(2·4 g.), *cyclo*hexenol (0·8 g.), unchanged peroxide (1·4 g.), "dimer" (0·4 g.), and undistilled residue (0·5 g.). After the lowest-boiling fractions had been heated with water at 115° in a sealed tube to hydrolyse any epoxy*cyclo*hexane present, only a small yield of *cyclo*hexane-1 : 2-diol, m. p. 104°, could be isolated from the product.

Action of the Hydroperoxide on cyclo*Hexen-3-ol.*—The alcohol (3·4 g.) and pure peroxide (3·5 g.) were heated together at 100° for 5 hours. The pale yellow liquid product was reduced with sodium sulphite solution and fractionated. The product consisted almost entirely of *cyclo*hexenol, but there were a small fraction (0·3 g.) of b. p. 100—105°/13 mm. and a higher-boiling residue (0·3 g.). The volatile fraction gave on heating with water in a sealed tube at 110° a small yield of *cyclo*hexane-1 : 2 : 3-triol (see below). No oxidation of *cyclo*hexenol to *cyclo*hexenone had occurred.

A similar mixture of alcohol and hydrocarbon in a quartz flask was shaken and simultaneously exposed to ultra-violet light at 35° in a nitrogen atmosphere. The product, after being freed from peroxide by shaking it with sodium sulphite, was fractionated : it consisted of *cyclo*hexenol (76%) and " dimeric " material, of b. p. 110°/13 mm. and above. No ketone was detected.

Action of Dilute Sulphuric Acid on the Hydroperoxide.—Crude, undistilled *cyclo*hexene hydroperoxide, derived by slow oxidation of *cyclo*hexene under feeble ultra-violet illumination (24 hours at 30—40°) and freed from unchanged *cyclo*hexene by distillation at 12 mm. pressure (4 g.), was mixed with N-sulphuric acid (20 c.c.) and kept at 40—45° for 1 week. The undissolved oil was collected with a little ether, and the clear aqueous layer then neutralised and evaporated to dryness. The residue yielded (*a*) by extraction with ethyl acetate crude *cyclo*hexanetriol, b. p. 115—120°/1 mm. (1 g.), which on crystallisation from ethyl acetate melted at 108—111° and on recrystallisation at 124° (Found : C, 54·65; H, 9·2. Calc. for $C_6H_{12}O_3$: C, 54·5; H, 9·15%), and (*b*) by acidification, followed by extraction with ether, a syrupy acidic oxidation product of high b. p. The water-insoluble oil when worked up gave *cyclo*pentene-1-aldehyde, b. p. 55—60°/13 mm. (0·6 g.) [dimedone, m. p. 123—124°; semicarbazone, m. p. 209° (Found : C, 54·5; H, 7·25; N, 26·7. Calc. for $C_7H_{11}ON_3$: C, 54·85; H, 7·25; N, 27·45%)], *cyclo*hexenol contaminated with a little unchanged peroxide, b. p. 65—70° (0·5 g.), and higher-boiling hydroxylic " dimeric " materials (1·6 g.). Repetitions of the experiment with hydroperoxide of correct or slightly low P.O.C. gave also *cyclo*hexanetriol (35—45% yield), *cyclo*hexenol (10—15%), water-insoluble hydroxylic oils, for the most part distillable (b. p. 70—100°/13 mm.) (*ca.* 10—15%), syrupy acidic material (*ca.* 10% yield), and always some *cyclo*pentenealdehyde. The yield of aldehyde increased considerably with decreasing P.O.C. of the hydroperoxide specimen but was never less than 2—3% even when derived from specimens of correct P.O.C.

Action of Water on the Hydroperoxide.—When the hydroperoxide (5·3 g.) of P.O.C. 17% was heated for 3 hours with water in a sealed tube at 115°, a brown oily layer (3·2 g.) and an aqueous layer resulted. The former when distilled gave *cyclo*pentene-1-aldehyde (0·8 g.) and about equal quantities of unchanged hydroperoxide, *cyclo*hexenol, and " dimeric " oil; the latter, on extraction with ethyl acetate, gave *cyclo*hexanetriol (1 g.) and a distillable hygroscopic syrupy acid (0·5 g.). The last of these was a non-homogeneos oxidation product, b. p. *ca.* 100°/2 mm. (Found : C, 58·65; H, 8·55%).

Action of Caustic Alkali on the Hydroperoxide.—The peroxide (9·3 g.) of P.O.C. 27·0%, when mechanically shaken with N-sodium hydroxide (150 c.c.) for 2 hours, dissolved to give a yellow solution. The product after having stood for 24 hours at room temprature gave on extraction with ether *cyclo*hexen-3-ol (6·6 g.; 82% yield). The alkaline liquor on acidification and extraction with ether gave a very small yield of adipic acid, m. p. 152° (mixed m. p. 152°), and some syrupy acid; a further amount of syrupy acid was obtained by continuous extraction with ether. The nature of this heterogeneous syrupy acid has been investigated by Hock and Gänicke (*loc. cit.*).

1-*Methyl*cyclo*hexene Hydroperoxide and its Transformation Products.*

1-*Methyl*cyclo*hexene Hydroperoxide,* 1-*Methyl*cyclo*hexene* 1 : 2-*Epoxide and* 1-*Methyl*cyclo*hexenol.*—Methyl*cyclo*hexene, b. p. 110—111° (90 g.), obtained by dehydration of 1-methyl*cyclo*hexanol in presence of a little iodine, was oxidised in a quartz flask at *ca.* 35°, as described for *cyclo*hexene (above). Absorption of gas occurred rapidly (1·5—2·5 l. per hour; 9,800 c.c. in 5½ hours), and the product gave on distillation at 15 mm. pressure unchanged methyl*cyclo*hexene (50 g.; nearly 60% recovery) and colourless, crude peroxide (39·1 g.). The latter gave on fractionation at 0·2 mm. : (i) b. p. 40—41°, P.O.C. 4·9% (11·8 g.), (ii) b. p. 52—58°, P.O.C. 20·95% (6·6 g.), (iii) b. p. 60—67°, P.O.C. 26% (5·0 g.), (iv) b. p. 67—70°, P.O.C. 24·0% (15·7 g.), and a " dimeric " residue, P.O.C. *ca.* 25% (15·0 g.).

The fraction (i), when freed from peroxide with sodium sulphite solution, was a volatile non-ketonic liquid (unreactive with the Girard reagent " T "), b. p. 65—67°/13 mm., having nearly the empirical composition of methyl*cyclo*hexenol but less than half its unsaturation (Found : C, 74·05; H, 10·95; iod. val., 103·9, 104·3. Calc. for $C_7H_{12}O$: C, 74·95; H, 10·7; iod. val., 226·9). This was a mixture of methyl*cyclo*hexenol (about 50%) with 1-methyl*cyclo*hexene 1 : 2-epoxide, and gave on hydrolysis with N-sulphuric acid (2·2 g. warmed with 15 c.c. of acid for 1 week at 40—45°) a 30% yield of *trans*-1-methyl*cyclo*hexane-1 : 2-diol (prisms, m. p. 84°, from light petroleum–chloroform; lit., m. p. 83·5°) (Found : C, 64·6; H, 11·0. Calc. for $C_7H_{14}O$: C, 64·6; H, 10·85%), together with a little methyl*cyclo*hexenol, b. p. 66—67°/13 mm. (0·3 g.) (see below) and a " dimeric " fraction, b. p. 130—132°/13 mm. (0·5 g.). Hydrolysis of a similar epoxide–alcohol fraction with water at 115° gave a similar result, but a smaller yield of diol.

The fraction (iii) consisted of nearly pure 1-*methyl*cyclo*hexene* 6 (with some 3)-*hydroperoxide* (P.O.C., 26. $C_7H_{12}O_2$ requires P.O.C., 25%), and fraction (iv) was only a little inferior in P.O.C. to (iii). Redistillation caused some secondary change, involving decomposition of the peroxide groups in a part of the material. The fraction of b. p. 64—67°/0·2 mm. so obtained had P.O.C. 99% of theory but was not quite pure (Found: C, 66·1; H, 9·75; active H, 0·85. $C_7H_{12}O_2$ requires C, 65·6; H, 9·4; active H, 0·78%).

When the hydroperoxide (3·6 g.) was shaken with 30% aqueous sodium sulphite (200 c.c.) for 3 hours and then similarly treated with fresh sulphite, reduction (less facile than with *cyclo*hexene hydroperoxide) occurred. The product, when extracted with ether, and dried, gave on distillation 1-*methyl*cyclo*hexen*-6(with some 3)-*ol* containing a little of a saturated secondary product (Found: C, 74·0; H, 10·1; iod. val., 206·3, 208·0. $C_7H_{12}O$ requires C, 74·95; H, 10·7%; iod. val., 226·7). The impure alcohol gave an oily 3 : 5-dinitrobenzoate from which a crystalline α-naphthylamine *complex*, m. p. 95—96° (Found: N, 9·35. $C_{24}H_{23}O_6N_3$ requires N, 9·35%), was obtained.

Hydrogenation of the hydroperoxide (11·6 g.; P.O.C. 22%) in alcohol by means of Adams's catalyst took place more slowly than with *cyclo*hexene hydroperoxide. After 18 hours, 3720 c.c. of hydrogen at N.T.P. had been absorbed (Calc. for $|^{=}_{0\cdot88}$ and 0·88 ·OOH group in peroxide of P.O.C. 22%: 3572 c.c.). The centrifuged product gave on distillation crude 1-methyl*cyclo*hexanol, b. p. 60—76°/13 mm. (Found: C, 71·85; H, 11·65. Calc. for $C_7H_{14}O$: C, 73·35; H, 12·3%), the *α-naphthylurethane* from which contained two difficultly-separable isomerides. Two crystallisations of the urethane from petroleum (b. p. 60—80°) gave a product, m. p. 123° (Found: C, 76·6; H, 7·65; N, 5·3. $C_{18}H_{21}O_2N$ requires C, 76·3; H, 7·4; N, 5·0%), which depressed the m. p. of the urethane of authentic 1-methyl*cyclo*hexane-3-ol (m. p. 123°; mixed m. p. 102°) but apparently consisted mainly of the urethane of 1-methyl*cyclo*hexan-2-ol (m. p. 154°; mixed m. p. 139°). Oxidation of the crude alcohol in aqueous acetic acid with chromic acid gave a ketone, b. p. 80—86°/60 mm., the semicarbazone from which melted at 175°, and after two crystallisations from methyl alcohol at 191° (Found: C, 56·6; H, 9·1. Calc. for $C_8H_{15}ON_3$: C, 56·8; H, 8·94%). This was identical with the semicarbazone of authentic 1-methyl*cyclo*hexan-2-one, m. p. 192° (mixed m. p. 191—192°). The mother-liquors of both urethane and semicarbazone each contained a second derivative in minor amount, difficultly purifiable, but in view of later observations (below), without doubt derived from 1-methyl*cyclo*hexan-3-ol and -3-one, respectively. It follows, therefore, that the hydroperoxide and methyl*cyclo*hexenol derived from 1-methyl*cyclo*hexene contained both the 6-substituted (major) and the 3-substituted (minor) isomerides.

Action of Dilute Sulphuric Acid on the Hydroperoxide.—The hydroperoxide (4 g.) was warmed to 45° for 100—120 hours with N-sulphuric acid (20 c.c.). The product contained an oily and an aqueous layer. The latter gave on neutralisation with alkali, evaporation, and extraction with ether, 1-*methyl*cyclo*hexane*-1 : 2 : 3-*triol*, b. p. 152—154°/1 mm., crystallising from ethyl acetate in small prisms, m. p. 95° (1·9 g.) (Found: C, 57·1; H, 9·55. $C_7H_{14}O_3$ requires C, 57·5; H, 9·6%), and the former on distillation at 13 mm. pressure gave three fractions, of b. p. 58°, 80—90°, and 114—120°, severally. The first of these fractions was a slightly impure ketone, $C_7H_{10}O$ (Found: C, 75·35; H, 9·3. Calc.: C, 76·3; H, 9·15%), recognised by its semicarbazone, m. p. 205° (Found: C, 57·3; H, 7·75; N, 24·9. Calc. for $C_8H_{13}ON_3$: C, 57·45; H, 7·8; N, 25·15%), and oxime, m. p. 91° (Found: C, 67·1; H, 8·7; N, 11·3. Calc. for $C_7H_{11}ON$: C, 67·15; H, 8·85; N, 11·2%), to be 1-acetyl*cyclo*pentene (Wallach, *Annalen*, 1909, **365**, 275, reports semicarbazone, m. p. 203—204°, and oxime, m. p. 91°). The higher-boiling fractions consisted of a little crude methyl*cyclo*hexenol containing unchanged peroxide and " dimeric " products. The neutral sodium salts gave on acidification and extraction with ether a syrupy, acidic product.

Action of Caustic Alkali on the Hydroperoxide.—When the hydroperoxide (6·4 g.) was shaken for 3 hours with N-sodium hydroxide (150 c.c.), kept overnight, and then warmed at 30° for 3 hours, an oil which proved to be a mixture of 6- and 3-hydroxy-1-methyl*cyclo*hexene separated and was collected in a little ether. The crude alcohol was re-treated with alkali to remove the last traces of peroxide, and then distilled. It boiled at 66—68°/13 mm. (Found: C, 74·5; H, 10·55. Calc. for $C_7H_{12}O$: C, 74·95; H, 10·7%); yield 89%. The alkaline solution gave on neutralisation, evaporation, and final extraction with ether of the acidified residue, a brown syrupy acid (1·0 g.), from which some large prisms of a monobasic *acid*, $C_7H_{10}O_2$, m. p. 207°, separated (Found: C. 66·6; H, 8·0; equiv., 125·7. $C_7H_{10}O_2$ requires C, 66·65; H, 8·0%; equiv., 126·0). The solid acid remained unattacked when shaken in alcohol with hydrogen and Adams's catalyst; it was, however, readily attacked by permanganate, giving thereby an acid of high oxygen content (?$C_7H_{12}O_6$), crystallising in minute stout plates, m. p. 69°, but obtained in too small amount to be adequately examined. The residual syrupy acid was heterogeneous, a minor part consisting of γ-acetylbutyric acid, isolated in the form of its hydrated semicarbazone, $C_7H_{13}O_3N_3,H_2O$, of m. p. 170° (decomp.) (slow heating), which became anhydrous at 100° (cf. Dieckmann, *Ber.*, 1912, **45**, 2704; Dupont, *Bull. Soc. chim. Belg.*, 1936, **45**, 57; *et al.*) (Found: C, 45·15; H, 6·9. Calc. for $C_7H_{13}O_3N_3$: C, 44·9; H, 7·0%), and the major part persisting as an intractably syrupy acid which was not further examined.

1 : 2-*Dimethyl*cyclo*hexene* 3-*Hydroperoxide and its Transformation Products.*

1 : 2-*Dimethyl*cyclo*hexene* 3-*Hydroperoxide,* 1 : 2-*Dimethyl*cyclo*hexene* 1 : 2-*Epoxide, and* 1 : 2-*Dimethyl*cyclo*hexen*-3-*ol.*—Dimethyl*cyclo*hexene, b. p. 136—137° (71 g.), obtained by dehydration in presence of iodine

of 1 : 2-dimethyl*cyclo*hexan-1-ol, formed from 2-methyl*cyclo*hexanone and methylmagnesium iodide, was oxidised at 23° in a quartz flask. In 95 mins., 5·8 l. (7·5 g.) of oxygen were absorbed. Distillation of unchanged hydrocarbon (41·5 g.) gave a residue of crude oxygenated products (35·6 g.) which on fractionation at 0·5 mm. pressure gave the fractions : (i) b. p. 40—50° (5·1 g.; P.O.C., 4·8%), (ii) b. p. 55—64° (8·8 g.; P.O.C., 19·4%); (iii) b. p. 64—69° (6·4 g.; P.O.C., 23·5%); (iv) b. p. 70—73° (6·1 g.; P.O.C., 22·3%), and a heterogeneous " dimeric " residue (6·0 g.; P.O.C., 9·8%). Of these fractions, (iii) and (iv) consisted of practically pure 1 : 2-*dimethyl*cyclo*hexane 3-hydroperoxide*, b. p. 67—70°/0·5 mm. (Found : C, 67·7; H, 9·9. $C_8H_{14}O_2$ requires C, 67·55; H, 9·9; P.O.C., 22·2%), and fraction (ii) also consisted mainly of hydroperoxide. Fraction (i), when it had been entirely freed from traces of unchanged hydroperoxide by treatment with sodium sulphite, and refractionated, gave a low-boiling portion containing 30—40% of a saturated component, and a higher-boiling portion (2·5 g.) of nearly pure dimethyl*cyclo*hexen-3-ol (iod. val., 191·5. Theory, 201·5), oxidisable to dimethyl*cyclo*hexen-3-one (see below). The lower-boiling portion was crude 1 : 2-dimethyl*cyclo*hexene 1 : 2-epoxide and gave on hydrolysis with N-sulphuric acid *trans*-1 : 2-dimethyl*cyclo*hexane-1 : 2-diol, m. p. 92° (0·5 g.) (Found : C, 66·4; H, 11·25. Calc. for $C_8H_{16}O_2$: C, 66·6; H, 11·2%). Refractionation at atmospheric pressure of the unchanged hydrocarbon, after it had been well dried with anhydrous magnesium sulphate (calcium chloride proved unsatisfactory), gave 4 g. of crude epoxide from which by hydrolysis with sulphuric acid the *trans*-diol, m. p. 92° (1·5 g.) was obtained.

Action of Dilute Sulphuric Acid on the Hydroperoxide.—The hydroperoxide (4·6 g.), when treated with N-sulphuric acid as above, gave a water-soluble fraction (2·0 g.) and a water-insoluble fraction (2·6 g.). The former gave on distillation at 0·5 mm. pressure 1 : 2-*dimethyl*cyclo*hexane*-1 : 2 : 3-*triol*, which crystallised from ethyl acetate–ether in colourless prisms, m. p. 109° (Found : C, 59·8; H, 10·1. $C_8H_{16}O_3$ requires C, 60·0; H, 10·1%); the latter gave on distillation (i) a ketonic fraction (free from aldehyde) of b. p. 74—80°/13 mm. (0·93 g.), (ii) an alcohol, identified as somewhat impure 1 : 2-dimethyl*cyclo*hexen-3-ol (see above), and (iii) a small " dimeric " residue. The ketone yielded a semicarbazone and an oxime which, when recrystallised from alcohol, melted respectively at 219° and 85°. These compounds proved on direct comparison to be identical with the corresponding derivatives (m. p.'s 221° and 86° respectively) of 1-acetyl-2-methyl*cyclo*pentene, the requisite ketone (b. p. 72—74°/13 mm.) being synthesised from 1 : 2-dimethyl*cyclo*hexene by successively ozonising it, heating the ozonide with water, and finally heating the resulting 1 : 4-diacetylbutane (b. p. 110°/13 mm.) with either N-sulphuric acid or alcoholic potassium hydroxide.

Action of Caustic Alkali on the Hydroperoxide.—The hydroperoxide was shaken with N-sodium hydroxide solution for 3—4 hours, and the mixture first allowed to stand overnight and then warmed to 30—40° for 2 hours. The product when worked up gave an alcohol (80% yield) and a syrupy acid (15—20% yield). The alcohol, after being freed from a little unchanged peroxide by renewed shaking with alkali, proved to be 1 : 2-*dimethyl*cyclo*hexen*-3-*ol*, b. p. 80—82°/13 mm. (Found : C, 75·35; H, 11·5; iod. val., 202. $C_8H_{14}O$ requires C, 76·1; H, 11·2%; iod. val., 201·5). This gave an α-*naphthylurethane*, m. p. 139—140° (Found : C, 77·0; H, 7·3. $C_{19}H_{21}O_2N$ requires C, 77·25; H, 7·15%), was oxidisable by chromic acid to 1 : 2-dimethyl*cyclo*hexene-3-one [semicarbazone, m. p. 224—225° (Kötz *et al.*, *Annalen*, 1913, **400**, 83, give m. p. 225°). Found : C, 59·4; H, 8·4. Calc. for $C_9H_{15}ON_3$: C, 59·6; H, 8·35%], and absorbed 1 mol. of hydrogen per mol. in presence of palladium–charcoal. The syrupy acid deposited (on one occasion only) a few colourless prismatic crystals, insufficient for adequate purification, of an acid, m. p. 196—197° (Found : C, 65·45; H, 7·95%), which was similar to, or possibly identical with, the acid of m. p. 207° derived similarly from 1-methyl*cyclo*hexene hydroperoxide; the main bulk, however, always consisted of γ-acetylbutyric acid [semicarbazone, m. p. 170°, identical with that obtained above in a corresponding way from 1-methyl*cyclo*hexene hydroperoxide (Found : C, 44·65; H, 6·9%)].

Rapid Decomposition of Peroxides.

cyclo*Hexene Hydroperoxide.*—When a few mg. of ferrous phthalocyanine were dropped into portions of 4 g. of fairly pure peroxide there was usually a flash of light, and always the liquid became warm and soon boiled. A little water separated, the liquid darkened in colour, and aldehydic vapour but no oxygen was evolved. Direct distillation of the liquid products when reaction subsided caused renewed reaction, with formation of much high-boiling material : it was better to extract the main products with light petroleum, leaving behind the catalyst and a little ether-soluble oxidation product. Distillation at reduced pressure then gave, first, a fraction of strong aldehydic odour and reaction, and later, fractions which contained much *cyclo*hexenol and unchanged peroxide. The aldehydic fraction, b. p. 60—62°/14 mm., was heterogeneous, giving a crude semicarbazone, m. p. 155—165°, containing two isomerides $C_7H_{11}ON_3$ (Found : C, 54·95; H, 7·25. Calc. : C, 54·85; H, 7·25%). By repeated recrystallisation from alcohol, the higher-melting component, m. p. 205°, was isolated in small yield and identified as *cyclo*pentene-1-aldehydesemicarbazone; the major component, however, could not be fully freed from its isomeride (m. p. 157—163°) and appeared to consist mainly of *cyclo*hexen-3-onesemicarbazone, m. p. 161°.

When the hydroperoxide was gradually heated in an open test-tube, standing in an oil-bath, very vigorous decomposition set in at about 120°, steam and volatile vapours being evolved, the latter containing *cyclo*pentene-1-aldehyde.

1-*Methyl*cyclo*hexene Hydroperoxide.*—Treatment of this peroxide with ferrous phthalocyanine as above caused development of heat, darkening in colour, and vigorous ebullition. The products, if freed from catalyst before being distilled, were almost completely distillable. The b. p. of the distillate rose progressively from 80°/13 mm. to 122°/11 mm. No exhaustive examination of the fractions was made, but much of the material consisted of methyl*cyclo*hexenol and unchanged hydroperoxide; the fractions boiling between 64° and 78° at 1 mm., however, contained a moderate proportion of ketone, which gave mixtures of two semicarbazones, (1) m. p. 207—208° (slow heating), identified as 1-methyl*cyclo*hexen-6-one semicarbazone (m. p. 207—208°; Wallach, *Annalen*, 1908, **359**, 303. Found : C, 57·5; H, 7·95. Calc. for $C_8H_{13}ON_3$: C, 57·45; H, 7·85%) by comparison with the semicarbazone of the ketone formed by oxidation of 1-methyl*cyclo*hexen-6-ol with chromic acid (mixed m. p. 207—208°), and (2) m. p. 198—200°, rather more readily soluble in alcohol than (1). This last compound appeared to be isomeric with both (1) and 1-acetyl*cyclo*pentenesemicarbazone (m. p. 207—208°; mixed m. p. 190—192°), and hence was probably 1-methyl*cyclo*hexen-3-one semicarbazone (m. p. 198°, 199—200°; Fargher and Perkin, J., 1914, **105**, 1362) (Found : C, 57·35; H, 8·0%).

1 : 2-*Dimethyl*cyclo*pentene Hydroperoxide.*—This peroxide when similarly decomposed with ferrous phthalocyanine gave a comparable heterogeneous product, the most volatile portion of which, b. p. 56—63°/1 mm., contained a ketonic component. This formed a semicarbazone, m. p. 219°, raised by recrystallisation from alcohol to 224—225°. This semicarbazone closely resembled in physical properties authentic 1 : 2-dimethyl*cyclo*hexen-3-one semicarbazone, m. p. 224—225°, derived by oxidation of 1 : 2-dimethyl*cyclo*hexen-3-ol with chromic acid; also it caused no depression of m. p. when heated with the latter. On the other hand, it depressed the m. p. of authentic 1-acetyl-2-methyl*cyclo*pentenesemicarbazone, m. p. 221° (mixed m. p. 209°).

Dimeric Products.

From cyclo*Hexene Hydroperoxide.*—From all autoxidation products there remained after distillation of the hydroperoxides at 0·2—1·0 mm. pressure a rather viscous, yellow, peroxidic oil which was partly distillable below 1 mm. pressure. The proportion of this polymeric residue varied considerably (from 25% to 40% of the total oxygenated material) with change in the conditions of oxidation, and increased markedly with prolongation of heating during the oxidation or distillation, and apparently also with prolongation of exposure to ultra-violet light. When the *crude* oxidation product was freed from active peroxide groups by reduction with sodium sulphite immediately the absorption of oxygen ended, the yield of dimeric material on subsequent distillation fell to 15—20%. Each time the pure hydroperoxide was distilled, a fresh small quantity of high-boiling residue was left; furthermore, when the carefully fractionated hydroperoxide was irradiated for several hours in an atmosphere of pure nitrogen, a considerable high-boiling, yellow residue remained on distillation.

When oxidation was conducted rapidly at *ca.* 30—35° and the monomeric products were removed as efficiently and rapidly as possible at pressures below 1 mm., the residue (*undistilled*) approximated in average composition to that required for the empirical formula $C_6H_{10}O_2$, as shown by analytical data from residues from three sources : (*a*) From normal oxidation (Found : 63·85; H, 8·95; P.O.C., 14·7%; iod. val., 122·0. Calc. for $C_{12}H_{20}O_4$: C, 63·2; H, 8·8; iod. val., for $|^{=}_{2}$, 222·8; P.O.C. for 2 ·OOH groups, 28·6%); (*b*) from irradiation of hydroperoxide in nitrogen (Found : C, 63·8; H, 9·0; P.O.C., 14·5%); (*c*) from redistillation of rectified hydroperoxide (Found : C, 63·75; H, 9·85; P.O.C., 12·65%). When the oxidation was conducted at higher temperatures (*e. g.*, 50—60°) or the process was unduly prolonged owing to use of feeble irradiation, or temperatures well above 70° were used in distilling off the monomeric hydroperoxide, then the P.O.C. of the residue was low, ranging down to 3%. Direct heating of the residue for a short time at 100° caused marked decrease in P.O.C. Since there was great difficulty in completely distilling the monomeric peroxide from the residue, whilst avoiding excessive heating, the figures for the P.O.C. of the polymeric material (distillation bath below 80°) were probably somewhat high.

Fractional distillation at 0·5 mm. pressure of a normal oxidation residue having P.O.C. 12·6% gave fractions of both varied boiling point (from 40° to 98°) and P.O.C., leaving a brown, almost peroxide-free mass in the still. Fractional distillation of a similar residue which had first been reduced to nearly zero P.O.C. with sodium sulphite gave on distillation fractions ranging in b. p. from 50° to 130° at 0·5 mm., and there remained a viscous yellow residue. A similar oxidation residue of average empirical composition corresponding nearly to $C_6H_{10}O_2$, and having P.O.C. 14·7%, and iod. val. 122, absorbed approximately 2 mols. of hydrogen in presence of Adams's catalyst, and then gave on distillation at 0·5 mm. pressure a little *cyclo*hexanol (10% yield), a little *cyclo*hexane-1 : 2-diol (1% yield), distillable " dimeric " materials ranging in b. p. from 60° to 120°, and an undistillable viscous residue. These high-boiling materials when reunited and extracted with hot water gave an extract (about ⅛ of the total) which on redistillation at 0·5 mm. pressure gave almost equal fractions of b. p. (*a*) 84° and (*b*) 96° severally. These fractions had each approximately the empirical composition $C_6H_{10}O$ [Found: (*a*) C, 73·65; H, 10·2; (*b*) C, 72·15; H, 10·1. Calc. for $C_6H_{10}O$: C, 73·4; H, 10·3%].

A normal oxidation residue (9·8 g.) when immediately extracted with hot water gave an aqueous extract containing a pale yellow, acid syrup (3·5 g.), leaving an undissolved neutral yellow oil (A). This syrup was divided by the action of dilute alkali into a neutral (B) and an acidic portion (C). All these fractions were in the main distillable, but none boiled constantly. The neutral fraction (A) boiled principally between 80° and 90° at 1 mm., and varied somewhat in composition from fraction to fraction and from preparation to preparation [*e.g.*, found for the main fractions of different peroxide-free preparations, (*a*) b. p. *ca.* 84°/1 mm., and (*b*) b. p. 80—86°/1 mm.: C, (*a*) 73·65, (*b*) 76·52; H, (*a*) 10·2, (*b*) 9·77. $C_{12}H_{20}O_2$ requires C, 73·4; H, 10·3%. $C_{12}H_{18}O$ requires C, 80·85; H, 10·2%]. The neutral, water-soluble fraction (B) had *M*, 320 (in benzene) and distilled for the most part at *ca.* 115°/13 mm. It was hygroscopic, reacted readily with benzoyl chloride, and was probably dihydroxylic (Found: C, 66·1; H, 9·9. $C_{12}H_{20}O_3$ requires C, 67·9; H, 8·5%). The hygroscopic, acidic, water-soluble fraction (C) had *M*, 231 (in benzene) and gave a main fraction of b. p. *ca.* 135°/13 mm. (Found: C, 56·7; H, 8·5%).

From 1-*Methyl*cyclo*hexene Hydroperoxide.*—The residue left when the hydroperoxide of 1-methyl*cyclo*hexene was distilled from the crude oxidation product (Found: C, 64·1; H, 9·0. Calc. for $C_7H_{12}O_2$: C, 65·6; H, 9·4%) gave on extraction with water a neutral, water-insoluble oil and an acidic, water-soluble syrup. Both these materials were almost wholly distillable but heterogeneous, boiling over the ranges 110—128°/1 mm. and 74—108°/1 mm. respectively. These were not further examined.

The above work has been carried out as part of the programme of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

THE BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION,
48, TEWIN ROAD, WELLWYN GARDEN CITY, HERTS.

[*Received, October* 18*th*, 1941.]