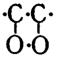
23. *The Course of Autoxidation Reactions in Polyisoprenes and Allied Compounds. Part II. Hydroperoxidic Structure and Chain Scission in Low-molecular Polyisoprenes.*

By Ernest Harold Farmer and Donald A. Sutton.

The oxidation by molecular oxygen of three polyisoprene hydrocarbons, dihydromyrcene, dihydrofarnesene, and squalene, has been examined. Dihydrofarnesene, within the limits of observation (up to 6·0% of absorbed oxygen), becomes peroxidised to the full extent of the oxygen intake, but retains its original unsaturation: hence the peroxidic groups are •OOH groups. Squalene and dihydromyrcene undergo extensive peroxidation, but almost from the beginning decay of the peroxide groups takes place side by side with peroxidation. Oxidised dihydromyrcene contains (*a*) oxygenated substances more or less peroxidic, and almost entirely monomeric, (*b*) oxygenated chain-scission products, and (*c*) untransformed peroxides of dihydromyrcene. Although the overall oxygen intake may be small, the stage of oxygenation reached in the molecules attacked may be well advanced, since distribution of the attack among the diolefinic molecules is uneven. The general nature of the oxygenated products and of the scission products has been investigated. From the complex oxygenated mixture there have been obtained by reduction of the peroxidic groups and subsequent fractionation hydroxydihydromyrcene, $C_{10}H_{17}(OH)$, possessing unimpaired the unsaturation of dihydromyrcene, and also (although in somewhat less pure form) dihydroxydihydromyrcene, $C_{10}H_{16}(OH)_2$.

The decrease of unsaturation in dihydromyrcene as it undergoes progressive oxidation is small compared with that which would take place if the absorbed oxygen became added at the double bonds (*e.g.*, to give cyclic peroxide groups  $\cdot\underset{|}{C}\cdot\underset{|}{C}\cdot$ / $O\cdot O$). During the decay of the peroxide groups the peroxidic oxygen becomes redistributed and enters at the unsaturated centres, which ultimately become the seats of chain scission. The loss of unsaturation produced by the entry of oxygen into those chains which remain unsevered is rather less than equivalent to the non-peroxidic oxygen (transformed peroxide) in the same undegraded chains, as estimated on the basis of two atoms of oxygen per double bond. The course of oxidation is indicated.

One of the most astonishing phenomena connected with the chemistry of rubber is the ease with which it absorbs progressively very small amounts of oxygen and suffers as a result drastic and progressive reduction of its molecular weight. The natural conclusion to be drawn is that the polyisoprene chains of the rubber are undergoing oxidative scission at one after another of their unsaturated centres, so that the original long hydrocarbon chains become divided into smaller and smaller fragments possessing oxygenated ends. Recent estimates of the molecular weight of rubber by viscosity and osmotic methods range from 240,000 to 360,000 for fractions of decreasing solubility in hydrocarbon solvents (Gee and Treloar, *Trans. Inst. Rubber Ind.*, 1941, **17**, 184; Bloomfield and Farmer, *ibid.*, 1940, **16**, 69). If we accept these figures and assume for the moment that two atoms of oxygen are sufficient to sever the hydrocarbon chains at a double bond, then an absorption of only 0·009—0·013% of oxygen (applied, of course, exclusively to scission reactions) should suffice to reduce the average molecular weight to one-half. If the observed reductions of molecular weight are solely to be ascribed to oxidative scission of the chains, then, provided oxygen-consuming side reactions are few, a fairly exact inverse proportionality may be expected to hold between the uptake of oxygen and the average molecular weight of the degraded rubber. The most striking reductions in the molecular weight per unit of oxygen absorbed must, of course, occur at the very early stages of oxidative fission, while the hydrocarbon chains are still very long, and in order to be able to follow effectively the quantitative relationship between these important reductions and the oxygen uptake, it is necessary to make experimental provision for the absorption, even distribution, and measurement of very minute quantities of oxygen.* Minute though the overall proportion of oxygen necessary to produce a substantial reduction in molecular weight appears in practice to be, however, there is no evidence to indicate that the scission reaction ever follows the course most economical in oxygen, *i.e.*,

$$\cdot CMe\colon CH\cdot + O_2 \longrightarrow \cdot COMe + \cdot CHO$$

or indeed represents the sole, or even the most important, line of reaction among the secondary changes which follow the initial peroxidation of the hydrocarbon. The chains of greatly reduced molecular weight are still much too long to permit of any satisfactory direct examination of the individual products for the purpose of confirming the reality of the oxidative scissions or of determining the mechanism connecting the initial peroxides with (1) the scission products and (2) other secondary products (if any) comparable with the alcohols, epoxides, ketones, and dimerides formed from *cyclo*hexene and methyl*cyclo*hexene (see Part I, preceding paper). For this reason, the autoxidative changes occurring in the low-molecular polyisoprenes, dihydromyrcene, dihydrofarnesene, and squalene, have been studied, and the present paper considers especially the character and point of entry of the peroxide groups, the tendency to chain scission, and the formation of oxygenated but unsevered chains.

The Formation and Character of Peroxide Groups.—The course of autoxidative reaction under ultra-violet irradiation which is shown by dihydromyrcene (I), dihydrofarnesene (II), and squalene (III)

$$\text{(I.)}\quad H\cdot[CH_2\cdot CMe\colon CH\cdot CH_2]_2\cdot H \qquad\qquad H\cdot[CH_2\cdot CMe\colon CH\cdot CH_2]_3\cdot H \quad \text{(II.)}$$

$$\text{(III.)}\quad H\cdot[CH_2\cdot CMe\colon CH\cdot CH_2]_3\cdot[CH_2\cdot CH\colon CMe\cdot CH_2]_3\cdot H$$

resembles in its primary aspects that pursued by various other olefinic substances. The absorbed oxygen forms peroxide groups, and these in lesser or greater degree decay, the peroxidic decompositions occurring side by side with the formation of new peroxide groups, so that the total content of peroxidic oxygen in the reaction mixture tends to fall seriously behind the oxygen intake. Small proportions of oxygen are lost by the formation of carbon dioxide and water, but these losses † are not very serious, especially in the early stages of reaction, so the peroxidic oxygen present at any moment represents some fraction, large or small, of the total oxygen in the system. The transformations of the peroxide groups, whether by isomerisation or by exercise of their energetic oxidative action on the rest of the molecule (or other molecules), constitute the chief autoxidative changes.

Now, in all studies of olefinic autoxidations described in the literature, the reasonably accurate measurement of the peroxide content in the unsaturated molecules and also that of the degree of unsaturation of the highly peroxidic products has been difficult and a source of error. The method of peroxide determination here employed is that referred to in Part I (p. 133), but special care has been necessary to avoid misleading values for the unsaturation of the peroxidised materials (see p. 145). In Fig. 1 the peroxide content is plotted against the oxygen content for dihydrofarnesene, dihydromyrcene, and squalene during the early stages of autoxidation. The behaviour of dihydrofarnesene is noteworthy in that all the absorbed oxygen up to an oxygen intake of 6·0% was found to be peroxidic and the hydrocarbon sustained no serious loss of unsaturation. The reaction mixture, therefore, contained at this point only unchanged hydrocarbon and dihydrofarnesene peroxides, and hence the latter could only have been of the hydroperoxide type. Dihydrofarnesene thus represented a very favourable example for the detailed examination of peroxidic structure, but owing to the great expense involved in the synthesis of the hydrocarbon (described elsewhere), no further study of the course of reaction could be undertaken. With squalene, absorption of oxygen up to 3·6% was observed. Here, the oxygen absorbed was found to be present entirely in peroxidic form at first, but decay of the peroxide soon set in, and at the end of the period of observation only about 57% of that formed had survived. The autoxidation product consisted

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* Careful measurements of the relation between oxygen uptake and the diminution of the molecular weight in the earliest stages of oxidation have been undertaken by Dr. J. Bolland and will later be described.

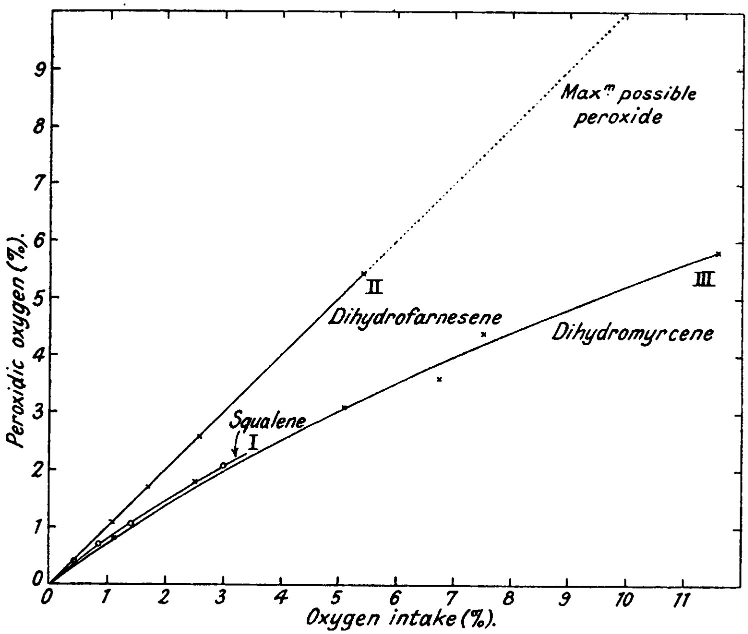
† Discussion of the significance of these is postponed, but owing to their low value the oxygen intake does not differ materially from the oxygen content as determined by analysis up to an advanced stage of reaction.

of unchanged hydrocarbon together with considerably oxygenated but largely non-peroxidic materials in which the original unsaturation had become very appreciably diminished. Autoxidation of dihydromyrcene was carried to an oxygen uptake of 11·6%, and of the peroxide thus formed only 50% survived in peroxidic form at the end of the period; repetitions of the oxidation gave very similar results. Since dihydromyrcene can be prepared with relative ease, it represents a convenient example for study.

General Character of the Autoxidation Products.—Pure dihydromyrcene (300 g.) was treated with oxygen in ultra-violet light (temperature 30—40°) for 45 hours, just over 7% by weight of oxygen being absorbed. About two-thirds of the hydrocarbon was found to have escaped oxidation, and of the remaining third about 4·5% consisted of relatively volatile scission products, and the residue of oxygenated dihydromyrcene possessed an *average* oxygen content of rather less than 25% (corresponding nearly to $C_{10}H_{18}O_3$). The scission products were distilled below 30° at 0·2 mm. pressure into a liquid-air trap, and the bulk of the unchanged hydrocarbon was driven over below 37° at the same pressure. The oxygenated residue was then fractionated below 70° by evaporative distillation at 10^{-3} mm. in a molecular batch still in an attempt to isolate some of the individual products.

Fig. 1.

Formation of Peroxide in Dihydrofarnesene, Squalene, and Dihydromyrcene.

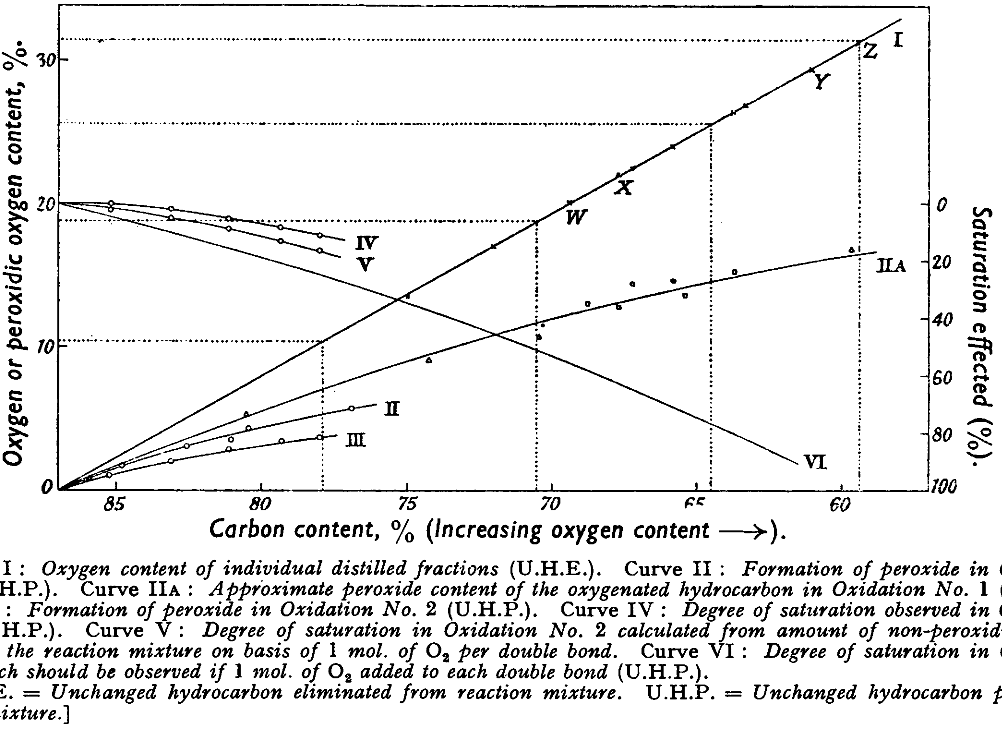


In general the moderate heating (below 45°) in high vacuum caused no very extensive damage to the peroxidised molecules. The peroxide contents of the less volatile portions were consistently high, and the unsaturation well marked. The active hydrogen values (dependent on both •OOH and •OH) were also very considerable, and tended to increase from the lower to the higher fractions, although there were considerable fluctuations from fraction to fraction. No satisfactory separation of the individual components of the mixture could, however, be effected. In order to improve the result if possible, refractionations of the more volatile distillates were carried out at 0·2 mm. pressure under a short column. The higher distillation temperatures, however, caused serious secondary change, so adding to the heterogeneity of the materials; and there was unmistakable evidence that very slow oxidative fission was occurring. Catalytic hydrogenation of the most promising fractions, followed by further fractional distillation under a column, did not give a homogeneous product.

In Fig. 2, Curve I, is shown the oxygen content, as determined by analysis, of a number of the fractions of undegraded oxygenated dihydromyrcene (selected over the range of oxygenation) plotted against the corresponding carbon content; the points *W*, *X*, *Y*, and *Z* on this curve, however, refer to the higher-boiling fractions of a second batch of oxidised dihydromyrcene. The oxygen values all fall with great precision on the oxygen content–carbon content curve (I) representing the formation of the oxidation stages $C_{10}H_{18}O$, $C_{10}H_{18}O_2$, $C_{10}H_{18}O_3$, $C_{10}H_{18}O_4$, from the hydrocarbon $C_{10}H_{18}$. All the distillate fractions had remained unpolymerised, and thus each consisted of one or more materials belonging to these * oxidation stages, except for the very earliest ones (unrepresented in the diagram) which still contained some unchanged hydrocarbon. It is noteworthy that oxidation can advance as far as $C_{10}H_{18}O_4$ (and indeed the material of fraction *Z* actually had this empirical composition) in spite of the fact that by far the larger proportion of the available hydrocarbon molecules escaped reaction. This very uneven attack of the molecules submitted to the action of oxygen suggests, not only that the oxygen enters the chain not less than one molecule at a time, but that the entry of a peroxide group facilitates further attack in the same molecule; moreover, our observations indicate that such an uneven attack is by no means unusual in the autoxidative reactions of olefinic substances, and hence it is probable that many statements in the literature purporting to refer to the *early* stages of oxidation really refer to fairly advanced stages so far as the molecules actually attacked are concerned. *Prolonged* heating of the peroxidised materials at temperatures above 100° under reduced pressure caused not only redistribution of oxygen, but some (low-molecular) polymerisation. Brownish-red, highly oxygenated, thermoplastic solids of trimeric or tetrameric complexity were so obtained.

FIG. 2.

Oxidation of Dihydromyrcene.



Curve I : *Oxygen content of individual distilled fractions* (U.H.E.). Curve II : *Formation of peroxide in Oxidation No.* 1 (U.H.P.). Curve IIA : *Approximate peroxide content of the oxygenated hydrocarbon in Oxidation No.* 1 (U.H.E.) Curve III : *Formation of peroxide in Oxidation No.* 2 (U.H.P.). Curve IV : *Degree of saturation observed in Oxidation No.* 2 (U.H.P.). Curve V : *Degree of saturation in Oxidation No.* 2 *calculated from amount of non-peroxidic oxygen present in the reaction mixture on basis of* 1 *mol. of* O_2 *per double bond.* Curve VI : *Degree of saturation in Oxidation No.* 2 *which should be observed if* 1 *mol. of* O_2 *added to each double bond* (U.H.P.).

[U.H.E. = *Unchanged hydrocarbon eliminated from reaction mixture.* U.H.P. = *Unchanged hydrocarbon present in reaction mixture.*]

The growth of peroxide groups in the hydrocarbon chains in comparison with the absorption of oxygen and the corresponding change in the unsaturation of the system deserves comment. The increase in the peroxide content (·O·O·) from stage to stage of a typical oxidation is shown for the undifferentiated mixture of unchanged and oxygenated hydrocarbon in curve II, Fig. 2. The same increase, but viewed in relation to just that portion (*i.e.*, about one-third) of the hydrocarbon which ultimately became successfully oxygenated, is shown approximately, for purposes of comparison with the oxygen intake (curve I), in curve IIA. The general level of the peroxide curve, however, varied materially from experiment to experiment in correspondence with small changes in the experimental conditions, and in Fig. 2 is shown a second peroxide-content curve (III) at a considerably lower level, that was obtained in a second

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* Whether or no any oxygenated derivatives containing odd numbers of oxygen atoms are present must depend on the occurrence or otherwise of intermolecular reactions such as $R{\cdot}OOH + {\cdot}C{:}C{\cdot} \longrightarrow R{\cdot}OH + {\cdot}\underset{O}{\underset{\vee}{C{\cdot}C}}{\cdot}$, and $R(OOH)_2 + {\cdot}C{:}C{\cdot} \longrightarrow R(OH){\cdot}OOH + {\cdot}\underset{O}{\underset{\vee}{C{\cdot}C}}{\cdot}$.

experiment in which oxidation was accelerated (and the temperature of reaction raised a little) by attaching a reflector to the quartz lamp used previously. The content of non-peroxidic oxygen, as obtained by subtracting the ordinates of (II) or of (III) from those of (I), is seen through most of the reaction to amount to quite a large fraction of the total absorbed oxygen, showing that secondary reaction soon becomes an important feature of the oxidation.

Corresponding to the increasing degree of peroxide decay as the reaction proceeds, there is a progressive diminution in the unsaturation of the system. This diminution is shown for the second of the above experiments, where peroxide decay (see curve III) was considerably more severe than usual, by curve IV of Fig. 2, and it will be seen that the decrease is small compared with that which would have occurred if the absorbed oxygen had been progressively added at the double bonds (2 atoms per double bond) as represented in curve VI. The unsaturation of the system cannot therefore be affected by the *primary* oxidation reaction (*i.e.*, peroxidation), and hence the peroxide groups can hardly be other than hydroperoxide groups which, on entering the carbon chain, leave the original double bonds intact. It would be expected from the evidence of autoxidative tendencies described in Part I that the degree of double-bond saturation brought about by the oxidation (cf. curve IV) would tend to show a quantitative correspondence with the non-peroxidic oxygen appearing in the reaction, on the basis of 2 atoms of non-peroxidic oxygen present per double bond lost * (curve V), since the important paths of decomposition open to the hydroperoxide groups all appear to involve concomitant oxidative saturation of a double bond rather than direct disintegration of the groups to leave the double bond intact [*e.g.*, as would occur if the decomposition $\mathrm{R{\cdot}CH(OOH){\cdot}CH{:}CH{\cdot}} \longrightarrow \mathrm{R{\cdot}CO{\cdot}CH{:}CH{\cdot}} + \mathrm{H_2O}$ were involved]. The occurrence of advanced stages of oxidation leading to chain scission and beyond, would, however, diminish the degree of this correspondence, since peroxidic oxidising power would then be used for post-saturation purposes. Experimentally, it was found that the degree of saturation effected did not reach equality with that to be expected on the basis of the non-peroxidic oxygen present, but amounted to about two-thirds of this (see curve V). Doubtless the appearance of chain-scission products from an early stage of the oxidation adequately accounts for the difference.

The Peroxidic Constitution.—In the case of peroxidised dihydrofarnesene (above), which suffered over the range of our observation no serious loss of unsaturation, reduction of the peroxide groups present would be expected to lead to the formation of a mixture of hydroxy- and dihydroxy-dihydrofarnesene [$\mathrm{R{\cdot}OOH} + 2\mathrm{H} \longrightarrow \mathrm{R{\cdot}OH} + \mathrm{H_2O}$; $\mathrm{R'(OOH)_2} + 4\mathrm{H} \longrightarrow \mathrm{R'(OH)_2} + 2\mathrm{H_2O}$]. If the peroxide groups in oxidised dihydromyrcene are similarly of hydroperoxidic character, as appears from the foregoing evidence to be the case, then those peroxidised molecules which have escaped secondary change, both in the actual oxidation and in any subsequent operations, should yield hydroxy- and dihydroxy-dihydromyrcenes on reduction, the former doubtless having one or other of the formulæ (A), (B), and (C), and the latter one or the other of (D) and (E) (see Part I), or alternatively either compound being a mixture of the appropriate isomerides.

$$\begin{array}{rcll}
\mathrm{CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH(OOH){\cdot}CMe{:}CH{\cdot}CH_3} & \longrightarrow & \mathrm{CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH(OH){\cdot}CMe{:}CH{\cdot}CH_3} & \text{(A)}\\
\mathrm{CH_2(OOH){\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_3} & \longrightarrow & \mathrm{CH_2(OH){\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_3} & \text{(B)}\\
\mathrm{CH_3{\cdot}CMe{:}CH{\cdot}CH(OOH){\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_3} & \longrightarrow & \mathrm{CH_3{\cdot}CMe{:}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_3} & \text{(C)}\\
\mathrm{CH_2(OOH){\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH(OOH){\cdot}CMe{:}CH{\cdot}CH_3} & \longrightarrow & \mathrm{CH_2(OH){\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH(OH){\cdot}CMe{:}CH_2{\cdot}CH_3} & \text{(D)}\\
\mathrm{CH_3{\cdot}CMe{:}CH{\cdot}CH(OOH){\cdot}CH(OOH){\cdot}CMe{:}CH{\cdot}CH_3} & \longrightarrow & \mathrm{CH_3{\cdot}CMe{:}CH{\cdot}CH(OH){\cdot}CH(OH){\cdot}CMe{:}CH{\cdot}CH_3} & \text{(E)}
\end{array}$$

Since in all our oxidations of dihydromyrcene a very considerable proportion of the peroxide groups always underwent secondary change during the oxidation itself, it was inevitable that any reduction products of the type (A)—(E), and especially dihydroxy-products such as (D) and (E), would be found in the reduced product mixed with other oxygenated materials of very similar empirical composition. Hence, separation of pure products would be difficult, and the yields of such separated materials poor. In practice, aluminium amalgam proved to be an effective reducing agent, but the low yield of hydroxy-dihydromyrcene to be expected was still further diminished owing to the difficulty experienced in recovering the alcoholic product completely from the alumina formed. Nevertheless, a monohydric alcohol, $\mathrm{C_{10}H_{17}{\cdot}OH}$, having two double bonds and one atom of active hydrogen per molecule, was duly isolated by fractional distillation, and also a corresponding dihydric alcohol, $\mathrm{C_{10}H_{16}(OH)_2}$. The former was with little doubt (A) or (C) or a mixture of both; the latter, however, on the scale of experimentation open to us, could not be freed entirely from more highly oxygenated materials of similar boiling point, and so the final fractionation product, although showing the correct active hydrogen content, had a somewhat low degree of unsaturation ($|^{=}_{1\cdot6}$) and a rather too high oxygen content. Repetition of the reduction with a further batch of oxidised dihydromyrcene gave exactly similar results. It is of some

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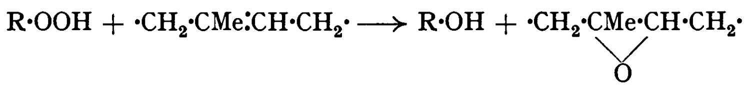
* Compare equations (A), (D), and (E), Part I.

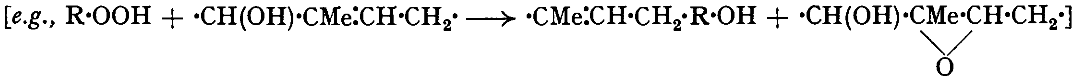
interest that the somewhat heterogeneous dihydric alcohol reacted readily and nearly quantitatively with standard lead tetra-acetate solution, and hence appears according to Criegee's rule to have consisted almost completely of α-glycols : therefore the major product is likely to have been (E) rather than (D), and the minor, more highly oxygenated component, a mono-olefinic triol such as $\mathrm{CH_3{\cdot}CMe(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CMe{:}CH{\cdot}CH_3}$ or $\mathrm{CH_3{\cdot}CMe{:}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}CMe(OH){\cdot}CH(OH){\cdot}CH_3}$.

The Products of Chain Scission.—The observations recorded in Part I indicate clearly that redistribution of the active oxygen of the hydroperoxide groups occurs largely or entirely as the direct result of the energetic oxidising action of the latter. In the absence of other reactive centres (*e.g.*, >CO, $\mathrm{{\cdot}\underset{O}{\underset{\diagdown\diagup}{C{\cdot}C}}{\cdot}}$) the chief oxidative attack occurs at the olefinic centres, and these accordingly first become saturated by oxygenation and ultimately, if reaction goes far enough, become the seats of chain scission. Two different types of scission reaction are to be distinguished, *viz.*, (*a*) in which break occurs at the double bond without any oxygenation of the α-carbon atoms, and (*b*) in which break occurs at the double bond but one or other of the α-carbon atoms becomes oxygenated and subsequently, if reaction goes far enough, split off. The first of these is initiated by an external peroxide or peracid group



$$\mathrm{R{\cdot}OOH + {\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot} \longrightarrow R{\cdot}OH + {\cdot}CH_2{\cdot}\underset{O}{\underset{\diagdown\diagup}{CMe{\cdot}CH}}{\cdot}CH_2{\cdot}}$$

and the second probably usually, but not necessarily always



$$[e.g.,\ \mathrm{R{\cdot}OOH + {\cdot}CH(OH){\cdot}CMe{:}CH{\cdot}CH_2{\cdot} \longrightarrow {\cdot}CMe{:}CH{\cdot}CH_2{\cdot}R{\cdot}OH + {\cdot}CH(OH){\cdot}\underset{O}{\underset{\diagdown\diagup}{CMe{\cdot}CH}}{\cdot}CH_2{\cdot}}],$$

by an α-situated hydroperoxide group.

All polyisoprene systems in our experience, and notably rubber, appear in the first place to give neutral scission products, and only later are these converted to a serious extent into acidic products containing carboxyl groups. Doubtless for polyisoprenes the neutral products have aldehydic and ketonic ends, and the former can probably absorb oxygen directly under illumination to form peracids and thence carboxylic acids, but it seems likely that the hydroperoxides themselves play a large part in the further oxidation of the scission products :

$$\mathrm{R{\cdot}OOH + R'{\cdot}CHO \longrightarrow R'{\cdot}CH(OH){\cdot}OOR \longrightarrow R'{\cdot}CO_2H + R{\cdot}OH}$$

The scission products unavoidably formed during the absorption of oxygen by dihydromyrcene contained a good deal of acetaldehyde, acetic acid, and acetone, together with water and some formic acid, showing that scission had occurred at both double bonds of the hydrocarbon, and with little doubt to some extent also at adjacent single bonds. The other degradation products were very mixed and difficult to identify. It is noteworthy, however, that no lævulic aldehyde or acid could be isolated or detected, partly, it is probable, because of its own autoxidisability, but largely, we believe, because the system $\mathrm{CH_3{\cdot}CMe{:}CH{\cdot}\overset{*}{C}H_2{\cdot}\overset{*}{C}H_2{\cdot}CMe{:}CH{\cdot}CH_3}$ is most readily attacked, and ultimately becomes most extensively hydroxylated, at one or both of the methylene groups marked,* leading, when the double bonds are severed, to enolisable ketols or hydroxy-aldehydes which are likely to undergo further degradation with rejection of acetic or formic acid.

Autoxidative scission reactions are of enormous practical significance in connexion with the perishing of rubber, the production of rancidity and offensive odours in oils and fatty acids, and the production of films from drying oils. It is of interest, therefore, to note that scission of peroxidised dihydromyrcene occurred, not only during the absorption of oxygen by the hydrocarbon and during subsequent heating (in distillation), but also on heating it with water, whereupon volatile products including acetaldehyde were formed. It is not impossible that these last fission products are to some extent to be traced to small amounts of ozonide (formed from the ozone usually present in irradiated oxygen) in the oxidation product, but in view of the observations recorded in Part I it would be expected that heating with water, analogously to heating with dilute sulphuric acid, would serve to cause slow hydrolysis of the hydroperoxide groups and promote oxidative attack at the double bonds.

Conclusions.

(1) The primary reaction involved in the oxidation of polyisoprenes (and probably of all olefinic substances in which the unsaturation is the structural feature which promotes reaction) is the formation of hydroperoxide groups on the α-methylene carbon atoms.

(2) In this primary reaction the unsaturation of the system remains unaffected.

(3) Secondary autoxidative changes, spontaneous or promoted by heat or other influences, set in with different degrees of facility in different substances and consist largely in the interaction of the hydroperoxide groups at the double bonds, which results mainly in oxidatively saturating the latter without severing them, although in a proportion of molecules reaction goes far enough to cause scission.

(4) In many substances the secondary reactions begin almost at the outset of reaction and proceed side by side with further peroxidation. The entry of oxygen into a molecule appears to facilitate further autoxidative attack in the same molecule, so that a low overall oxygen intake is compatible with advanced oxidation in some of the molecules.

(5) Reduction of the peroxide groups in those peroxidised dihydromyrcene molecules which have escaped secondary reaction yields alcohols which retain intact the original unsaturation of the hydrocarbon.

(6) Chain scission takes place with some facility at the double bonds, with formation of fragments with oxygenated ends, but subsidiary scission appears to occur also at certain of the single bonds adjacent to the double bonds.

EXPERIMENTAL.

Dihydromyrcene.—Myrcene was prepared from bay oil (*Pimenta acris*) by the method of Power and Kleber (*Pharm. Rundschau*, 1895, **13**, 60). The well-washed hydrocarbon, fractionated over sodium, had b. p. 51—53°/10 mm., $d_{4°}^{20°}$ 0·7981, $n_D^{22°}$ 1·468, and gave at once with maleic anhydride the adduct, m. p. 34° (Diels, m. p. 34—35°), and the latter by hydrolysis the corresponding dicarboxylic acid, m. p. 122° (Diels, m. p. 122—123°). Yield, 20% of original oil. The myrcene was reduced with sodium and alcohol as described by Semmler and Mayer (*Ber.*, 1911, **44**, 2010), except that 162 g. of sodium and a total of 1820 c.c. of absolute alcohol per 500 g. of hydrocarbon sufficed to ensure complete reduction. The well-washed hydrocarbon, after being twice distilled over sodium through a Widmer column, boiled at 52·5—55°/11 mm. (Found : C, 86·8; H, 13·1. Calc. for $C_{10}H_{18}$: C, 86·9; H, 13·1%). It had $d_{4°}^{20°}$ 0·7809, $n_D^{23°}$ 1·4495, and gave a tetrabromide, m. p. 87—88° (Found : Br, 69·8. Calc. : Br, 69·8%). Semmler and Mayer report $d_{4°}^{15°}$ 0·7802, $n_D^{20°}$ 1·4507 and m. p. of tetrabromide, 87°. To ensure that the dihydromyrcene contained no myrcene, a portion (10 g.) was heated at 100° for 10 mins. with maleic anhydride. No visible reaction occurred, no trace of adduct could be found, and the recovered hydrocarbon had the original physical constants.

Squalene.—A fraction of the liver oil of *Symnorhinus lichia* of b. p. 225—235°/1 mm. was used, after it had been well washed with caustic alkali and with water. This pale yellow hydrocarbon contained oxygenated impurities as Heilbron *et al.* had observed (J., 1926, 1630) with similar specimens, but these were expeditiously and satisfactorily removed by adsorption on activated alumina (21 g. of hydrocarbon dissolved in 1000 c.c. of light petroleum run slowly through a column of alumina 33 cm. × 2 cm., and the chromatogram developed by 150 c.c. of light petroleum). The purified oil (Found : C, 87·8; H, 12·3. Calc. for $C_{30}H_{50}$: C, 87·7; H, 12·3%) had $d_{4°}^{20°}$ 0·8562, $n_D^{23°}$ 1·494, $[R_L]_D$ 139·5, and showed like Heilbron's product an appreciable molecular exaltation (1·5 units). The cause of this exaltation will be considered in a later paper.

Dihydrofarnesene.—This tri-isoprene was synthesised from geraniol as will be described later.

Determination of Unsaturation.—For the determination of unsaturation in oxidised polyisoprenes the iodine-value method is convenient but has the disadvantage that organic peroxides react with the potassium iodide used as reagent, and by liberating iodine cause low unsaturation values to be obtained. Direct hydrogenation is an alternative, but owing to the necessity of determining the peroxide content separately and subtracting the hydrogen equivalent of the peroxide ($R{\cdot}OOH + H_2 \longrightarrow R{\cdot}OH + H_2O$) from the total quantity of hydrogen absorbed, the method is subject to a double error, which renders it too inaccurate for use with small quantities of material, although it enables very useful near approximations to be made with specimens of several g. or more. Determination of unsaturation by bromine addition has proved unsatisfactory, and determination by means of standard solutions of peracids is unsuitable owing to the tendency of these oxidising agents to cause chain scission with consumption of additional peroxide. Of all these methods, as conducted under various recommended procedures, the iodine value has proved to be most satisfactory for general analytical control, but the magnitude of the error even under standard conditions of working is variable owing to differences in the reducibility of different peroxides. For the reactive hydroperoxides of low-molecular polyisoprenes and *cyclo*hexene peroxides, unsaturation values found by the iodine value method are estimated to be 4—5% too low, but not more, provided the final titration after the addition of potassium iodide be conducted rapidly, and in a solution well diluted with water. The existence of this error renders the direct observation of very small changes in unsaturation in the early stages of peroxidation (*e.g.*, in the case of dihydrofarnesene) unreliable. The unsaturation values used in plotting curves (IV)—(VI), Fig. 2, are uncorrected ones, and hence the degrees of saturation there shown are considered to be about 5% higher than the actual value.

General Oxidation Procedure.—The unsaturated hydrocarbon, together with a diluent if desired, was placed in a 2-necked Pyrex flask and connected through a calcium chloride tube to a gas burette and reservoir containing oxygen. The air in the flask was displaced with oxygen, and the flask placed 15 cm. from an ultra-violet lamp (Hanovia U.V.S. 500) and shaken mechanically. The heat radiated from the lamp kept the flask at a temperature between 35° and 40°. Usually after an induction period of about 1 hr. absorption of oxygen began and was allowed to proceed until the desired amount of oxygen had been absorbed, or until absorption seriously slackened. For determination of the peroxide formed, or the saturation effected from stage to stage in the oxidation, suitable portions of material were withdrawn with a pipette through one of the necks of the flask, the level of the gas burette being noted before and after the interruption, and the air unavoidably admitted to the flask during the interruption being replaced by oxygen before oxidation was continued. Invariably in the course of the oxidation a little water was eliminated, and some carbon dioxide formed. Since neither of these up to the point of oxidation desired interfered with the absorption of oxygen or caused any very serious error in the measurement of the oxygen intake (as confirmed by numerous comparisons of the latter with the oxygen content of the products), no steps were taken to remove them as they were formed.

Oxidation of Squalene.—The purified squalene (10 c.c.; 8·45 g.), dissolved in 100 c.c. of pure dry benzene, was oxidised at 35—40° for 105 mins. after the induction period (60 mins.) had ended. Withdrawals of 2 c.c. of the solution were made from time to time, and the peroxide content of each sample determined. The change in the peroxide content of the solution of hydrocarbon up to an average oxygen intake of 3·6% of its weight is shown in Fig. 1, curve I. The product was freed from solvent by distillation of the latter at reduced pressure, and the residual oil (7·6 g.) was divided into two parts by fractional dissolution in methyl alcohol. The alcohol-insoluble portion (5·5 g.) was nearly free from oxygen [Found : C, 87·2; H, 12·3; O (by diff.), 0·5. Calc. for $C_{30}H_{50}$: C, 87·7; H, 12·3%] and consisted mainly of unchanged squalene, whilst the alcohol-soluble portion consisted of oxygenated squalene having an average empirical composition of $C_{30}H_{50}O_{3\cdot65}$, and a peroxide content (6·5%) slightly more than half the total average oxygen content.

Oxidation of Dihydrofarnesene.—This triene hydrocarbon (4·14 g.) was oxidised without a diluent, withdrawals of samples (3) being made at intervals as before. The hydrocarbon, which had been kept in a stoppered bottle for 1 week after purification, contained at the outset 0·22% of peroxidic oxygen, and finally after absorption of 6·0% of its weight of oxygen (leading to an average empirical formula of $C_{15}H_{26}O_{0.82}$) contained 6·0% of peroxidic oxygen. The unsaturation, determined by iodine values, diminished inappreciably, and had finally decreased by 4·8% (<0·8% corrected) of the initial figure.

Oxidation of Dihydromyrcene.—Dihydromyrcene (100 g.) was oxidised without a diluent during 42½ hours, samples being withdrawn at intervals for peroxide determination. The total oxygen intake amounted to 11·6% of the weight of hydrocarbon taken. The variation of the peroxide content as the absorption of oxygen proceeded is shown in Fig. 1, curve III.

A further quantity of hydrocarbon (300 g.) was oxidised as before, absorption of oxygen being continued until it became slow. A total of 16,550 c.c. of oxygen was absorbed in 45 hours. The product (nearly 323 g.) was placed in a 2-necked flask surmounted by a Widmer column and connected to a liquid-air trap. The flask was very gently warmed at 0·2 mm. pressure to drive over (i) very volatile products (*A*) which collected in the liquid-air trap (27·6 g.), (ii) volatile materials (*B*) of b. p. 30—37° (205 g.), leaving (iii) a residue (*C*) (85 g.) in the flask.

The fraction (*A*) evolved no gases when it was warmed slowly up to 10°, and it could be distilled at atmospheric pressure under a short Vigreux column without great loss of volatile matter. There were obtained (*a*) acetaldehyde (dimedon derivative, m. p. 140—141°; mixed m. p. 140—141°. Found : C, 70·5; H, 8·5. Calc. for $C_{18}H_{26}O_4$: C, 70·55; H, 8·55%), (*b*) a volatile liquid, b. p. 30—74°, which yielded on refractionation more acetaldehyde, a quantity of acetone (2 : 4-dinitrophenylhydrazone, m. p. 126°; mixed m. p. 126°. Found : N, 23·9. Calc. for $C_9H_{10}O_4N_4$: N, 23·5%), (*c*) a fraction, b. p. 60—90°, which separated into two layers and on refractionation gave water, some acetic acid (*p*-bromophenacyl ester, m. p. 84°; mixed m. p. 85°. Found : C, 46·35; H, 3·6; Br, 31·65. Calc. for $C_{10}H_9O_3Br$: C, 46·7; H, 3·5; Br, 31·1%), a small amount of pungent volatile acid of b. p. *ca.* 100°, which satisfied Rimini's and other qualitative tests for formic acid, and a quantity of unidentified volatile liquid material, and (*d*) 22 g. of crude hydrocarbon [added to (*B*)]. The total yield of the volatile scission products including acetaldehyde, acetic acid, water, and acetone and unidentified products amounted to 4·5—8% of the weight of hydrocarbon actually oxygenated (*ca.* 100 g.).

The fraction (*B*) (205 g. + 22 g.) was found on refractionation to consist almost entirely of unchanged dihydromyrcene, but it contained some non-ketonic oxygenated material. The total proportion of unchanged dihydromyrcene, including the first of the sub-fractions of (*C*, I) (see below) was estimated to be 200 g.

The fraction (*C*) was a light yellow, fairly mobile oil of strong peroxidic character (peroxidic oxygen, 9·62%) which was first partly distilled at 10^{-3} mm. pressure in a batch still, the most volatile portion, (*C*, I) (16·65 g.; peroxidic oxygen, 0·94%), being collected in a liquid-air trap, the intermediate portion (*C*, II) (29·7 g.; peroxidic oxygen, 12·9%) distilling at 60—70° as a slightly viscous, yellowish oil, leaving a residue (*C*, III) (25·85 g.; peroxidic oxygen, 12·2%) of yellow viscous liquid.

The fraction (*C*, I) was divided by fractional distillation under a short column into 5 fractions ranging in b. p. from 56° to 104°/12 mm. The first (2 g.) consisted of dihydromyrcene, the second, containing only 6·05% of oxygen, was of rather lower unsaturation than dihydromyrcene (179·8 g. equiv. to $2I_2$) and consisted of dihydromyrcene mixed with an oxygenated substance which appeared to be an alcohol (? tertiary) since it reacted with 3 : 5-dinitrobenzoyl chloride to give a red oil, which in turn gave a thick red oil with α-naphthylamine. The third was acidic, containing a little formic acid which had been produced by thermal degradation during the distillation; when the formic acid was removed, the highly oxygenated residue had barely half the unsaturation of dihydromyrcene (148·6 g. equiv. to I_2) and was non-ketonic [Found : C, 75·0; H, 11·55; O (by diff.), 13·45%]. The fourth fraction was also non-ketonic but was more highly oxygenated than the third and slightly more unsaturated [Found : C, 72·0, 72·05; H, 10·65, 10·9; O (by diff.), 17·35, 17·05%; 138·7 g. equiv. to I_2]. The fifth (1·1 g.), which was very viscous and apparently somewhat polymerised by heat, was discarded.

A portion (18 g.) of the fraction (*C*, II) was divided by fractional distillation at 10^{-3} mm. pressure in the batch still into five portions (*C*, II, *a*—*e*), four of which were distillates ranging in b. p. from 40° to 50°, and the fifth the residue. The following data were obtained : *C*, II*a* : C, 65·85; H, 9·85; O (by diff.), 24·3; O (peroxidic), 11·7; active H, 0·62%; *C*, II*b* : O (peroxidic), 11·7%; *C*, II*c* : C, 67·2; H, 10·2; O (by diff.), 22·6; O (peroxidic), 14·6; active H, 0·74%; *C*, II*d* : C, 63·7; H, 9·8; O (by diff.), 26·5; O (peroxidic), 15·5%; *C*, II*e* : C, 63·65; H, 9·5; O (by diff.), 26·85%. A little volatile material (1·2 g.) of low peroxidic content (1·6%) also collected in the liquid-air trap.

Of the above fractions *C*, II*c* was reduced catalytically by means of Adams's catalyst, which was removed by centrifuging. The saturated and peroxide-free product was divided by fractional distillation into 6 fractions (i—vi). Of these (i), b. p. 82—85°/12 mm. (0·15 g.), closely resembled (ii) and was not separately examined; (ii) was a sweet-smelling oil, b. p. 86—90°/12 mm. (Found : C, 73·0; H, 12·95%), which reacted with 3 : 5-dinitrobenzoyl chloride to give a red oil, but this gave no solid adduct with α-naphthylamine (cf. Reichstein, *Helv. Chim. Acta*, 1926, **9**, 799); (iii) was a nearly odourless oil, b. p. 96—98°/12 mm. [Found : C, 72·6; H, 12·7; O (by diff.), 14·7%], which probably contained as minor component an alcohol of formula $C_{10}H_{22}O$, since it reacted with 3 : 5-dinitrobenzoyl chloride to give a red oil, forming with α-naphthylamine a somewhat unstable and difficultly crystallisable *derivative*, m. p. 91—96° (15% yield) (Found : N, 8·8. $C_{17}H_{24}O_6N_2,C_{10}H_9N$ requires N, 8·9%), but since its oxygen content greatly exceeds that of hydroxydihydromyrcene (O, 10·4%) which has approximately the same b. p., the major component must contain together with hydroxyl a volatile oxygen-containing group such as epoxy; (iv) was an odourless oil, b. p. 104—114°/12 mm. (Found : C, 70·95; H, 11·95%); (v) was a viscous oil, b. p. 117—122°/12 mm., of high oxygen content and hydroxylic character which probably consisted mainly of dihydric alcohol, $C_{10}H_{22}O_2$, and in part of an α-glycol, since about half of it reacted with lead tetra-acetate (Found : C, 68·4; H, 11·55. Calc. for $C_{10}H_{22}O_2$: C, 68·96; H, 12·6%).

The residue (*C*, III) remaining in the still was a pale yellow syrup of average composition $C_{10}H_{18}O_{3\cdot2}$ (see p. 141) and peroxide content 12·2% (*i.e.*, an average of 0·71 ·OOH group per mol.). A portion (14·3 g.) was hydrogenated in presence of Adams's catalyst, and the saturated hydroxylic products were divided into ten portions by fractional distillation, leaving a tiny residue. All fractions were yellow oils, and the 4 lowest ones, b. p. 40—110°/10 mm., resembled those derived by hydrogenation of fraction (*C*, II*c*) above; the higher ones, *C*, III, vii—ix, b. p. 75—146°/1 mm., all had the empirical composition $C_{10}H_{19\cdot8}O_{2\cdot5}$, and the highest (*C*, III, x) and the residue had the composition $C_{10}H_{18\cdot5}O_{2\cdot3}$ and $C_{10}H_{17\cdot5}O_{2\cdot26}$ respectively. It is to be deduced, therefore, that the sub-fractions vii—ix have taken up an average of 1·8 atoms of hydrogen and lost 0·7 atom of oxygen per mol., and hence the peroxidic parent material must have contained an average of 0·9 and *ca.* 0·7 ·OOH group per mol. The final fractions (x and residue), however, have respectively gained $H_{0\cdot5}$ and lost $H_{0\cdot5}$ per mol. and respectively lost $O_{1\cdot0}$ and $O_{0\cdot95}$ per mol. This doubtless marks the beginnings of the post-saturation autoxidative changes leading to chain scission and its accompaniments of water and carbon dioxide elimination, and in the residue possibly of polymerisation.

Advanced Stage of Oxidation.—Oxidation of 100 g. of dihydromyrcene gave after exhaustive distillation of the less oxygenated fractions at reduced pressures and at bath temperatures below 100° a residue in the still having a composition of nearly $C_{10}H_{18}O_4$ and containing 11% of peroxidic oxygen [Found : C, 59·7 : H, 9·0; O (by diff.), 31·3. $C_{10}H_{18}O_4$ requires C, 59·4; H, 9·0; O, 31·6%]. In another oxidation of hydrocarbon the final fraction obtained by distillation had an empirical formula of nearly $C_{10}H_{18}O_{3\cdot7}$ [Found : C, 61·0; H, 9·1; O (by diff.), 29·9%] and peroxidic oxygen 15·1%.

Action of Prolonged Heating.—The oxidation product from 29 g. of dihydromyrcene (7·1% oxygen intake) was freed from unchanged hydrocarbon, and fractionally distilled at successive pressures of 13 mm., 1—2 mm., and 10^{-3} mm., the temperature of the heating bath being allowed to rise to about 150° in each case. The residue in the still (*ca.* 5 g.) formed a brownish-red, resinous mass, which was extensible on warming, and able to yield fine threads. It had approximately the composition $C_{10}H_{18}O_2$, and from cryoscopic determinations had between tri- and tetra-meric complexity [Found : C, 70·2; H, 9·3; O (by diff.), 20·5%; *M* (in benzene), 610. $C_{10}H_{18}O_2$ requires C, 70·6; H, 10·6; O, 18·8%; *M*, 170]. The polymerisation process had thus involved material loss of both hydrogen and oxygen, probably largely as water.

Reduction of Hydroperoxido- and Dihydroperoxido-dihydromyrcene.—Dihydromyrcene (300 g.) was oxidised in a quartz flask to an oxygen intake of only 1%, and then immediately reduced by aluminium amalgam in moist ether containing a little alcohol. Reaction was vigorous at first, and after 24 hours all peroxidic material had disappeared. The ethereal solution, freed from alumina and from the large bulk of unchanged dihydromyrcene, gave only a moderate yield of reduced product, which by re-extraction of the alumina was finally raised to 60% of that expected. Since extensive secondary autoxidation processes unavoidably accompany peroxidation, it was necessary to select the desired products by careful fractional distillation.

Fractions were finally obtained of b. p. (i) 55—58°/12 mm. (1·7 g.), (ii) 58—83°/12 mm. (0·9 g.), (iii) 90—103°/12 mm. or 70—76°/1 mm. (1·8 g.), (iv) 80—96°/1 mm. (0·1 g.), (v) 96—106°/1 mm. (0·5 g.), (vi) 115°/1 mm. (0·5 g.), and (vii) residue (1 g.). The fractions (i) and (ii) both contained some dihydromyrcene, but (iii) was free from hydrocarbon and had the correct composition and characteristics for *hydroxydihydromyrcene* (Found: C, 77·75; H, 11·35; active H, 0·65; $|^{=}_{1\cdot95}$. $C_{10}H_{18}O$ requires C, 77·9; H, 11·7; active H, 0·65%; $|^{=}_{2\cdot0}$). The alcohol reacted with 3 : 5-dinitrobenzoyl chloride to give a thick red oil, affording a non-crystalline complex with α-naphthylamine.

The fraction (iii) approximated in composition and characteristics to *dihydroxydihydromyrcene* (Found: C, 68·85; H, 10·45; active H, 1·05; $|^{=}_{1\cdot6}$. $C_{10}H_{18}O_2$ requires C, 70·6; H, 10·6; active H, 1·18%; $|^{=}_{2\cdot0}$), but clearly contained a little more highly oxygenated material. The diol reacted with N/10-lead tetra-acetate (Consumption: 96·5% of theory) and probably consists mainly of a 1 : 2-diol of formula (E) (p. 143).

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