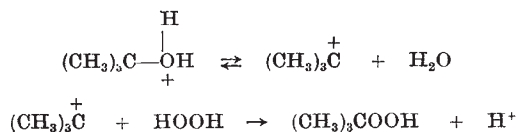## Preparation of Alkyl Hydroperoxides

ALKYL hydroperoxides have been prepared by the action of hydrogen peroxide on : (1) alkyl sulphates, R_2SO_4, in the absence (for example, $R = \text{but}$)[1] or presence (for example, $R = \text{Et}$)[2] of alkali ; (2) tertiary alcohols in the presence of a trace of concentrated sulphuric acid[3] ; (3) triphenylmethyl halides[4,5]. All these reactions may be interpreted as involving nucleophilic attack of the HOOH molecule or HOO^- ion on a carbon atom according to the general equation :

$$HO\ddot{O}:\overline{} + CR_3\overline{}X \rightarrow HOO\text{—}CR_3 + \ddot{X}.$$
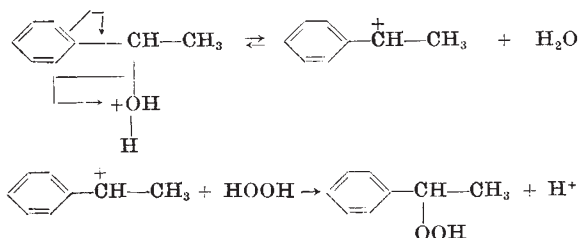
Both oxygen atoms in the resultant peroxide thus originate in the hydrogen peroxide molecule. This must necessarily be the case in reaction (3), but it is also thought to apply in reactions of types (1) and (2). The reaction may proceed by either of the two established mechanisms of nucleophilic substitution (the S_N1 and S_N2 mechanisms), and variation in constitutional and environmental factors will produce the usual effects[6]. Characteristic stereochemical consequences may be expected ; for example, partial or complete racemization should accompany mechanism S_N1.

Criegee and Dietrich[3] state that primary and secondary alcohols do not react under the conditions of reaction (2). This reaction probably occurs readily with tertiary alcohols because inductive and hyperconjugative electron release by the alkyl groups, in conjunction with acid catalysis, facilitates the production of a carbonium ion which is then attacked by the hydrogen peroxide to give the alkyl hydroperoxide (the S_N1 mechanism).

$$
\begin{array}{c}
\overset{\displaystyle H}{\underset{\displaystyle +}{(CH_3)_3C\text{—}OH}} \rightleftarrows (CH_3)_3\overset{+}{C} + H_2O
\end{array}
$$

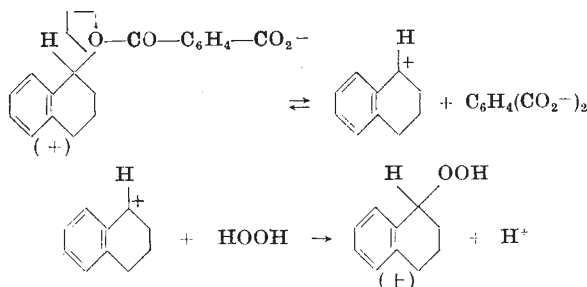$$(CH_3)_3\overset{+}{C} + HOOH \rightarrow (CH_3)_3COOH + H^+$$

The reaction should, therefore, not be restricted to tertiary alcohols, but should apply to any alcohol which will yield carbonium ions under the conditions of reaction. This has been confirmed by the preparation of 1-phenylethyl hydroperoxide from 1-phenylethyl alcohol under Criegee and Dietrich's conditions. In this case, the S_N1 reaction is facilitated by electron release by the phenyl group ; in sec.-butyl alcohol this factor is absent, and this alcohol is unreactive under the same conditions[7].

$$\text{[structure] CH—CH}_3 \rightleftarrows \text{[structure]}\overset{+}{C}H\text{—CH}_3 + H_2O$$
$$\downarrow +OH$$
$$H$$

$$\text{[structure]}\overset{+}{C}H\text{—CH}_3 + HOOH \rightarrow \text{[structure]—CH—CH}_3 + H^+$$
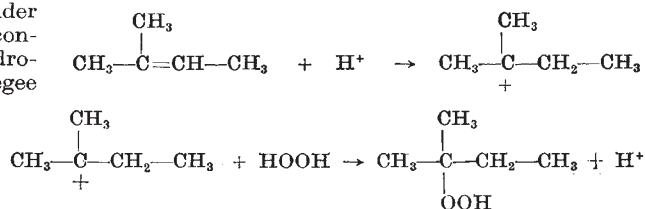$$\underset{OOH}{}$$

Hydroperoxides should also be produced by other types of compounds which are capable of the production of alkyl cations. Thus a carboxylic ester which readily undergoes alkyl–oxygen fission should be perhydrolysed to give an alkyl hydroperoxide and a carboxylic acid. This reaction has been established in the case of the hydrogen phthalate of 1 : 2 : 3 : 4-tetrahydro-1-naphthol. This ester has been shown to have a tendency to react by an alkyl–oxygen fission mechanism : for example, the optical activity of the alcohol obtained by hydrolysis of the ester decreases with decreasing nucleophilic power of the hydrolytic reagent, and the alcohol itself readily forms a sulphone with p-toluenesulphinic acid[8]. It has now been found that when 1 : 2 : 3 : 4-tetrahydro-1-naphthyl hydrogen phthalate is dissolved in 90 per cent hydrogen peroxide containing sodium bicarbonate, 1 : 2 : 3 : 4-tetrahydro-1-naphthyl hydroperoxide, identical with the product obtained by the autoxidation of 1 : 2 : 3 : 4-tetrahydronaphthalene, soon separates in good yield ; if the optically active ester is used, the inactive hydroperoxide results. It has been shown that 1 : 2 : 3 : 4-tetrahydro-1-naphthol does not react under similar conditions and thus cannot be an intermediate in the reaction. The reaction would therefore appear to proceed by a unimolecular alkyl–oxygen fission mechanism, as follows :

$$\text{[reaction scheme: tetrahydronaphthyl phthalate} (+) \rightleftarrows \text{tetrahydronaphthyl cation} + C_6H_4(CO_2^-)_2$$
$$\text{tetrahydronaphthyl cation} + HOOH \rightarrow \text{tetrahydronaphthyl hydroperoxide (OOH)} (+) + H^+\text{]}$$

The addition of a proton to an olefine will also produce an alkyl cation, which should react with hydrogen peroxide to lead to the formation of an alkyl hydroperoxide. This has been confirmed in the case of 2-methylbut-2-ene. This olefine, when stirred for 18 hr. with 90 per cent hydrogen peroxide in the presence of a trace of concentrated sulphuric acid, gives a good yield of tert.-amyl hydroperoxide. The mechanism of this reaction is hence thought to be as follows :

$$
\begin{array}{c}
\overset{\displaystyle CH_3}{CH_3\text{—}C{=}CH\text{—}CH_3} + H^+ \rightarrow \overset{\displaystyle CH_3}{\underset{\displaystyle +}{CH_3\text{—}C\text{—}CH_2\text{—}CH_3}}
\end{array}
$$

$$
\begin{array}{c}
\overset{\displaystyle CH_3}{\underset{\displaystyle +}{CH_3\text{—}C\text{—}CH_2\text{—}CH_3}} + HOOH \rightarrow \overset{\displaystyle CH_3}{\underset{\displaystyle OOH}{CH_3\text{—}C\text{—}CH_2\text{—}CH_3}} + H^+
\end{array}
$$

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[7] Davies and Foster (unpublished).
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