314. *Organic Peroxides. Part I. The Preparation of Alkyl Hydroperoxides from Hydrogen Peroxide.*

By A. G. Davies, R. V. Foster, and A. M. White.

The preparation of alkyl hydroperoxides by the reaction of concentrated hydrogen peroxide with (*a*) alcohols, (*b*) carboxylic esters, (*c*) 2-butyl sodium sulphate, and (*d*) olefins has been investigated. It is suggested that reactions of (*a*), (*b*), and (*c*), and the corresponding reactions of alkyl halides, involve nucleophilic substitution by hydrogen peroxide usually by a unimolecular mechanism, *viz.* :

$$R\overset{\curvearrowright}{-}X \overset{\text{slow}}{\rightleftharpoons} R^+ + X^- \qquad R^+ + HO{\cdot}OH \xrightarrow{\text{fast}} RO{\cdot}OH + H^+$$

In the reaction of olefins the alkyl cation is formed by protonation, the subsequent step being as above.

Two types of reaction for the preparation of alkyl hydroperoxides are known. The first, the autoxidation of a hydrocarbon, occurs most readily at the α-position to a benzene ring (*e.g.*, as in 1 : 2 : 3 : 4-tetrahydronaphthalene) or a double bond (*e.g.*, as in *cyclo*hexene), and its mechanism has been interpreted as that of a homolytic chain reaction (Farmer, Bloomfield, Sundralingham, and Sutton, *Trans. Faraday. Soc.*, 1942, **38**, 348).

The second method involves the reaction of hydrogen peroxide with (*a*) tertiary alcohols in the presence of a trace of concentrated sulphuric acid (Criegee and Dietrich, *Annalen*, 1948, **560**, 135), (*b*) alkyl sulphates ($RR'SO_4$) in the presence (*e.g.*, $R = R' = Me$; Baeyer and Villiger, *Ber.*, 1901, **34**, 738) or absence (*e.g.*, $R = Bu^t$, $R' = H$; Milas and Surgenor, *J. Amer. Chem. Soc.*, 1946, **68**, 205) of alkali, or (*c*) triarylmethyl halides (*e.g.*, triphenylmethyl chloride; Wieland and Maier, *Ber.*, 1931, **64**, 1205). The preparation of alkyl hydroperoxides by the action of hydrogen peroxide on certain secondary and tertiary alcohols and on the carboxylic esters and olefins derived from them is now reported.

In Criegee and Dietrich's preparation, the tertiary alcohol is treated with 90% hydrogen peroxide containing a trace of concentrated sulphuric acid at room temperature for some hours. It is stated (Criegee and Dietrich, *loc. cit.*; Criegee, *Fortschr. chem. Forsch.*, 1950, **1**, 508—566, especially p. 530) that primary and secondary alcohols are unreactive under these conditions. We have now shown, however, that, although simple saturated aliphatic secondary alcohols (*e.g.*, butan-2-ol, and 3 : 3-dimethylbutan-2-ol) can be recovered unchanged after such treatment, (secondary) α-substituted benzyl alcohols, as well as tertiary alcohols are converted into the corresponding alkyl hydroperoxides. *tert.*-Butyl, *tert.*-amyl, 1-*iso*butyl-1-methylpropyl, 1-phenylethyl, diphenylmethyl, and 1 : 2 : 3 : 4-tetrahydro-1-naphthyl hydroperoxides have been prepared in good yield by this method. In all cases reaction takes place in the presence of sulphuric acid, but some alcohols react in the presence of the weaker acid, formic acid, or even in the absence of catalyst. The alkyl groups above are arranged in the approximate order of increasing reactivity. The optically active 1 : 2 : 3 : 4-tetrahydro-1-naphthol gives the optically inactive hydroperoxide. All the hydroperoxides named above, except 1-*iso*butyl-1-methylpropyl, have been previously described.

In the study of the reactivity of hydrogen peroxide towards carboxylic esters, we have used chiefly the readily available alkyl hydrogen phthalates because their sodium salts form a homogeneous solution in concentrated hydrogen peroxide. When 1 : 2 : 3 : 4-tetrahydro-1-naphthyl or diphenylmethyl hydrogen phthalate is dissolved in 90% hydrogen peroxide containing sodium hydrogen carbonate, the corresponding hydroperoxide soon separates in good yield. From the optically active 1 : 2 : 3 : 4-tetrahydro-1-naphthyl ester the inactive hydroperoxide is formed. Only a small amount of 1-*iso*butyl-1-methylpropyl hydroperoxide could be isolated, and no reaction occurred with 1-phenylethyl hydrogen phthalate. Reaction mixtures from methyl or 1-methylheptyl hydrogen phthalate are unstable, but about 70% of the starting material can be recovered after 4 hr. A poor yield of 1 : 2 : 3 : 4-tetrahydro-1-naphthyl hydroperoxide was obtained by stirring the acetate with hydrogen peroxide containing formic acid; the reaction is not therefore restricted to hydrogen phthalates.

The yields of methyl, ethyl, and *iso*propyl hydroperoxides obtained by treatment of the corresponding dialkyl sulphates with strongly alkaline hydrogen peroxide are reported to be low (Eggersglüss, *Angew. Chem.*, 1951, **61**, 72); but treatment of *tert.*-butyl and *tert.*-amyl hydrogen sulphates with 30% hydrogen peroxide gives good yields of a mixture of the corresponding alkyl hydroperoxide and dialkyl peroxide (Milas and Surgenor, *J. Amer. Chem. Soc.*, 1946, **68**, 205, 643). We were unable to obtain 1-methylpropyl hydroperoxide by treating 1-methylpropyl sodium sulphate with neutral 90% or alkaline 30% hydrogen peroxide.

To support the postulation (see Discussion) of the existence of intermediate carbonium ions in the preparations of alkyl hydroperoxides from alcohols and esters, attempts were made to obtain the same products by the addition of hydrogen peroxide to olefins. 2-Methylbut-2-ene with concentrated hydrogen peroxide containing a trace of concentrated sulphuric acid gave *tert.*-amyl hydroperoxide; the hydrogen atom therefore adds to the least alkyl-substituted end of the double bond: $CH_3{\cdot}CH{:}CMe{\cdot}CH_3 + HO{\cdot}OH \longrightarrow CH_3{\cdot}CH_2{\cdot}CMe_2{\cdot}O{\cdot}OH$. Similarly the olefin derived from 3 : 5-dimethylhexan-3-ol (probably 3 : 5-dimethylhex-2-ene) reacts to form 1-*iso*butyl-1-methylpropyl hydroperoxide, but *cyclo*hexene is unchanged by such treatment.

Criegee and Dietrich (*loc. cit.*) have used the *p*-nitrobenzoates to characterise alkyl hydroperoxides. We prefer, however, to use the previously undescribed 1-alkyl hydrogen 1-monoperphthalates (o-$RO_2{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$) because estimation of the free-acid group gives confirmation of the equivalent weight of the hydroperoxide. These crystalline derivatives are readily prepared by the use of phthalic anhydride in the presence of pyridine (under which conditions *tert.*-alcohols do not react). Decomposition occurs when the peresters are heated above their melting points, phthalic acid and acetone being among the products of decomposition of the *tert.*-butyl perester. It has also been shown that these compounds catalyse the polymerisation of styrene. These problems are being further investigated. 1-*tert.*-Butyl hydrogen 1-monopersuccinate is also described. Unfortunately the 1-phenylalkyl hydroperoxides do not form stable esters; when this work was carried out, no satisfactory derivatives of such compounds were available.

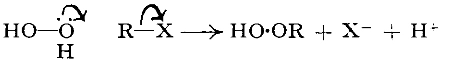
DISCUSSION

The S_N1 reactions of alkyl halides (Hughes, Ingold, and their co-workers, *J.*, 1933—1952; cf. *Quart. Reviews*, 1951, **5**, 245) and the unimolecular alkyl–oxygen fission reactions of carboxylic esters and of alcohols (Day and Ingold, *Trans. Faraday Soc.*, 1941 **37**, 686; Kenyon and his co-workers, *J.*, 1942—1952) all proceed by the general mechanism :

$$R{-}X \underset{}{\overset{\text{slow}}{\rightleftharpoons}} R^+ + X^- \qquad R^+ + Y^- \xrightarrow{\text{fast}} R{-}Y$$

where X = Cl, etc., $R'\cdot CO_2$ or HO ($R'\cdot CO_2\overset{+}{H}$ and $\overset{-}{H}O_2$ under acid conditions), respectively. A study of the relative rates of such reactions permits the arrangement of the various groups R in the following approximate order of increasing reactivity by unimolecular mechanism : Me, Et, Pr^i, Bu^t, CHPhMe, $CHPh_2$.

It is now suggested that all the preparations of alkyl hydroperoxides by the reaction of hydrogen peroxide with alkyl derivatives (R—X; where X = Cl, HO, or $H_2\overset{+}{O}$, $R'\cdot CO_2$, $R'SO_4$) involve nucleophilic attack by the HO·OH molecule or $HO\cdot O^-$ ion according to the general equation :



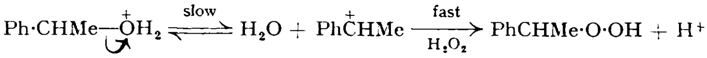
$$\underset{\displaystyle H}{HO{-}O} \quad R{-}X \longrightarrow HO\cdot OR + X^- + H^+$$

and that this takes place usually by a unimolecular mechanism of the type described in the summary.

When the critical complex of such a reaction involves the appearance of charges, this will be favoured by the high polarity of 90% hydrogen peroxide (dielectric constant, 97 at 0°). A rapid bimolecular attack by un-ionised hydrogen peroxide upon the types of molecules which do undergo reaction would appear to be improbable in view of the low basicity of the hydrogen peroxide molecule (Evans and Uri, *Trans. Faraday Soc.*, 1949, **45**, 224).

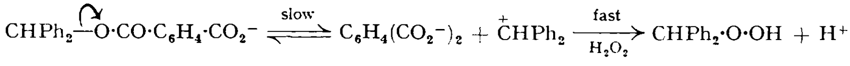
Triphenylmethyl halides thus react readily with hydrogen peroxide (Wieland and Maier, *loc. cit.*; Pinazzi, *Compt. rend.*, 1948, **226**, 929) probably because electron release by the phenyl groups promotes the reactivity by the S_N1 mechanism. Substitution of a $-T$ group in the *ortho-* or *para*-position in the benzene rings would tend to negate the $+T$ effect of the phenyl groups; thus *p*-nitrotriphenylmethyl chloride is less reactive towards hydrogen peroxide but the reaction is catalysed by stannic chloride which aids the removal of the chloride anion by the formation of the $SnCl_5^-$ ion (Bartlett and Cotman, *J. Amer. Chem. Soc.*, 1950, **72**, 3095).

The reactivity of the various alcohols and carboxylic esters towards hydrogen peroxide follows the sequence given above for the reactivity by the unimolecular mechanism. Again then, such reactions would appear to be unimolecular substitution reactions, *e.g.*



$$Ph\cdot CHMe{-}\overset{+}{O}H_2 \overset{\text{slow}}{\rightleftharpoons} H_2O + Ph\overset{+}{C}HMe \xrightarrow[H_2O_2]{\text{fast}} PhCHMe\cdot O\cdot OH + H^+$$

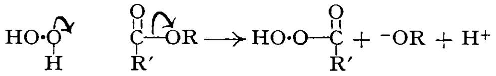
and



$$CHPh_2{-}O\cdot CO\cdot C_6H_4\cdot CO_2^- \overset{\text{slow}}{\rightleftharpoons} C_6H_4(CO_2^-)_2 + \overset{+}{C}HPh_2 \xrightarrow[H_2O_2]{\text{fast}} CHPh_2\cdot O\cdot OH + H^+$$

(the $B_{AL}1$ mechanism : Day and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 686; Bunton, Hughes, Ingold, and Meigh, *Nature*, 1950, **166**, 680). This conclusion is supported by the observation that optically active 1 : 2 : 3 : 4-tetrahydro-1-naphthol and its hydrogen phthalate yield the inactive hydroperoxide in both cases. In the mechanism postulated the intermediate carbonium ion would be planar, and racemisation would occur at this stage.

The position of the methyl and simple saturated secondary alkyl groups in the sequence of reactivity by a unimolecular mechanism suggests that unimolecular alkyl–oxygen fission reactions of methyl hydrogen phthalate and 2-octyl hydrogen phthalate would be slow and reaction by an acyl–oxygen fission mechanism more probable. Such a reaction with hydrogen peroxide would lead to the formation of a peracid and an alcohol :



$$\mathrm{HO{\cdot}\underset{H}{O}} \quad \mathrm{\underset{R'}{\overset{O}{C}}{-}OR} \longrightarrow \mathrm{HO{\cdot}O{-}\underset{R'}{\overset{O}{C}}} + {}^{-}\mathrm{OR} + \mathrm{H^+}$$

Unfortunately the instability of such reaction mixtures rendered impossible the isolation of any products of reaction.

The reactivity of *tert.*-alkyl sulphates towards the weakly nucleophilic neutral hydrogen peroxide and of methyl and ethyl sulphates towards the more strongly nucleophilic alkaline hydrogen peroxide, may be indicative of the S_N1 and S_N2 mechanisms respectively, both proceeding by alkyl–oxygen fission. The low reactivity of the simple secondary alkyl halides by either of these two mechanisms (Gleave, Hughes, and Ingold, *J.*, 1935, 226) may afford an explanation of our failure to isolate any *sec.*-butyl hydroperoxide from the reaction between sodium *sec.*-butyl sulphate and hydrogen peroxide

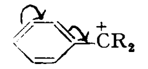
If the postulation of an intermediate carbonium ion is correct, then processes other than dissociation which will produce a carbonium ion in a medium of hydrogen peroxide might also be expected to lead to the formation of alkyl hydroperoxides. An example of this is provided by the preparation of *tert.*-amyl hydroperoxide by the reaction between 2-methylbut-2-ene and hydrogen peroxide in the presence of a trace of sulphuric acid :

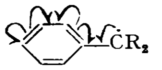
$$\mathrm{CMe_2{:}CHMe} + \mathrm{H^+} \longrightarrow \mathrm{\overset{+}{C}Me_2{\cdot}CH_2Me} \qquad \mathrm{\overset{+}{C}Me_2{\cdot}CH_2Me} + \mathrm{HO{\cdot}OH} \longrightarrow \mathrm{HO{\cdot}O{\cdot}CMe_2{\cdot}CH_2Me} + \mathrm{H^+}$$

The direction of addition of the hydrogen peroxide and the fact that *cyclo*hexene is unreactive under similar conditions, are both in agreement with the known influence of substituents on such a reaction mechanism (Gwyn Williams, *Trans. Faraday Soc.*, 1941, **37**, 749).

The range of alkyl hydroperoxides which can be prepared by the alkylation of hydrogen peroxide is thus more extensive than has previously been supposed. The reaction of alcohols perhaps affords the most convenient available method of preparation, but appears to be restricted to alcohols with a reactivity approximately equal to or greater than *tert.*-butyl alcohol. The danger of explosion which may accompany such reactions (Criegee and Dietrich *loc. cit.*) is probably caused by the instability of the hydroperoxide towards the acid catalyst, and can be mitigated to some extent by the use of the weakest acid capable of catalysing the reaction. The scope of the methods of preparation described here coincides to some extent with that of the autoxidation of hydrocarbons, because the $+T$ groups which will stabilise an alkyl cation (*e.g.* A), will also stabilise the corresponding alkyl radical (*e.g.* B). However a $-T$ group, which would not stabilise an alkyl cation to any appreciable extent, will nevertheless stabilise the corresponding free radical (Ingold, *Trans. Faraday Soc.*, 1934, **30**, 52), and thus the autoxidation reaction may be applicable to a compound RH, whose corresponding derivatives RX might be unreactive by the ionic mechanism suggested here.

(A)





(B)

EXPERIMENTAL

Light petroleum refers to the fraction with b. p. 40—60°. The preparation and resolution of 1 : 2 : 3 : 4-tetrahydro-1-naphthol and its derivatives have been described previously (Davies and White, *J.*, 1952, 3300).

Analysis for Peroxidic Oxygen.—The amount of hydroperoxide in mixtures was roughly estimated as follows : A known weight (approx. 0·20 g.) of the impure hydroperoxide was dissolved in glacial acetic acid (10 c.c.), and potassium iodide (1·0 g.) was added. Next morning the liberated iodine was estimated with sodium thiosulphate solution, and comparison made with a blank solution. The accuracy of the method is within approx. ±4%.

Hydrogen Peroxide.—Unstabilised 85—90% hydrogen peroxide was supplied by Messrs. Laporte Chemicals Ltd., Luton. Precautions were taken to minimise the effect of a possible explosion in reactions with this material; detonation never took place, but vigorous decomposition occurred on a few occasions, caused apparently by instability of the organic peroxide produced under the (frequently acid) experimental conditions.

Preparation of Hydrogen Perphthalates and Persuccinates.—The following details illustrate the method of preparation of the 1-alkyl hydrogen 1-monoperphthalates and 1-monopersuccinates. A mixture of *tert.*-butyl hydroperoxide (9 g.), phthalic anhydride (14·8 g.), and pyridine (11·8 g., 1·5 mols.) was set aside for 12 hr. at room temperature, most of the phthalic anhydride dissolving. After 10 min. at 65—68° the clear solution was cooled, diluted with an equal volume of acetone, acidified (Congo-red) with 6N-hydrochloric acid, and then diluted with water. The deposited hydrogen perphthalate was recrystallised from ether–light petroleum giving 1-tert.-*butyl hydrogen* 1-*monoperphthalate* (20·2 g.) as stable, white crystals, m. p. 104—104·5° (decomp.) (Found: C, 61·0; H, 6·0%; equiv., 236. $C_{12}H_{14}O_5$ requires C, 60·5; H, 5·9%; equiv., 238).

Reaction between 85—90% *Hydrogen Peroxide and Alcohols.*—(i) tert.-*Butyl alcohol.* The alcohol (5 c.c.) was added to hydrogen peroxide (5 c.c.) containing concentrated sulphuric acid (0·05 c.c.), at 0°. After 6 hr. at room temperature, water (15 c.c.) was added, the upper organic layer extracted with light petroleum, and the extract washed and dried (Na_2SO_4). Distillation yielded *tert.*-butyl hydroperoxide (4·8 g.), b. p. 50—54°/45 mm., n_D^{20} 1·3985, n_D^{25} 1·3968. By reaction with phthalic anhydride in the presence of pyridine (see above) this yielded 1-*tert.*-butyl hydrogen 1-monoperphthalate, m. p. 104° (decomp.) (Found: equiv., 238. Calc. for $C_{12}H_{14}O_5$: equiv., 238). A similar reaction with succinic anhydride in the presence of pyridine (experiment by Mr. K. J. HUNTER) gave, in good yield, 1-tert.-*butyl hydrogen* 1-*monopersuccinate* as a stable white solid (from ether–light petroleum), m. p. 58—59° (Found: C, 50·0; H, 7·3%; equiv., 195. $C_8H_{14}O_5$ requires C, 50·5; H, 7·4%; equiv., 190).

From a similar reaction mixture, in which 98% formic acid (0·05 c.c.) was used as catalyst, after 72 hr. most of the *tert.*-butyl alcohol (3·5 c.c.) was recovered by salting out with potassium carbonate, but a residue of *tert.*-butyl hydroperoxide (0·30 g.), b. p. 37—38°/19 mm., was obtained, from which was prepared the hydrogen phthalate, m. p. and mixed m. p. 103—104·5° (decomp.). In the absence of any catalyst, the unchanged alcohol was recovered after 21 days and shown by analysis to be free from peroxidic material.

(ii) tert.-*Amyl alcohol.* After 6 hr.' stirring and 16 hr. at room temperature, a mixture of the alcohol (10 c.c.), hydrogen peroxide (10 c.c.), and concentrated sulphuric acid (0·02 c.c.) yielded *tert.*-amyl hydroperoxide (4·36 g.), b. p. 50—51°/20 mm., n_D^{20} 1·4154 (Found: C, 57·9; H, 11·6. Calc. for $C_5H_{12}O_2$: C, 57·7; H, 11·6%). From this hydroperoxide (1 g.), 1-tert.-*amyl hydrogen* 1-*monoperphthalate* (1·5 g.) was obtained as glassy rhombs, m. p. 87—89° (decomp.) (Found: C, 61·4; H, 6·6%; equiv., 252. $C_{13}H_{16}O_5$ requires C, 61·9; H, 6·3%; equiv., 252). By reaction of the hydroperoxide (1 g.) with *p*-nitrobenzoyl chloride (1·79 g.) in the presence of pyridine (1·14 g.), tert.-*amyl* p-*nitroperbenzoate* was obtained as pale yellow needles (from aqueous ethanol or light petroleum), m. p. 48·5—49·5° (Found: C, 57·1; H, 6·0; N, 5·8. $C_{12}H_{15}O_5N$ requires C, 56·9; H, 5·9; N, 5·5%).

(iii) 3 : 5-*Dimethylhexan*-3-*ol.* The alcohol, prepared by Clarke's method (*J. Amer. Chem. Soc.*, 1908, **30**, 1144), had b. p. 150—151°/754 mm., 72—74°/50 mm., n_D^{20} 1·4267, n_D^{25} 1·4241. The alcohol (10 c.c.), hydrogen peroxide (10 c.c.), and concentrated sulphuric acid (0·10 c.c.) were stirred for 6 hr., giving 1-iso*butyl*-1-*methylpropyl hydroperoxide* (8·3 g., 88% yield), b. p. 51—52°/2 mm., n_D^{20} 1·4350, n_D^{25} 1·4331, d_4^{25} 0·895 (Found: C, 66·2; H, 12·6. $C_8H_{18}O_2$ requires C, 65·7; H, 12·4%). There was a small unidentified viscous residue (0·85 g.). An attempt to prepare the hydroperoxide via the alkyl hydrogen sulphate (Milas and Surgenor, *loc. cit.*) gave only an olefin, b. p. 113—114°. Doering and Zeiss (*J. Amer. Chem. Soc.*, 1950, **72**, 147) reported an olefin, b. p. 112—115°, as a by-product from the reductive cleavage of 1-*iso*butyl-1-methylpropyl hydrogen phthalate with methylmagnesium bromide.

The hydroperoxide (63 g.), phthalic anhydride (64 g.), and pyridine (51 g.) gave the *hydrogen* 1-*monoperphthalate* (102 g.) as a stable white crystalline solid (from ether–light petroleum), m. p. 87—90° (decomp.), the melting point being dependent upon the rate of heating (Found: C, 65·9; H, 7·8%; equiv., 294. $C_{16}H_{22}O_5$ requires C, 65·3; H, 7·5%; equiv., 294).

(iv) 1-*Phenylethanol.* The alcohol (2 g.) was stirred for 6 hr. at 5—10° with hydrogen peroxide (10 c.c.) and concentrated sulphuric acid (0·02 c.c.). Water (20 c.c.) was then added and the product obtained by ether extraction, washing of the extract with dilute sodium hydrogen carbonate solution and distillation. The slightly yellow oil (3·5 g. from 2 preparations),

b. p. 60°/0·05 mm., contained approx. 95% of the hydroperoxide, estimated volumetrically. Aqueous sodium hydroxide (5 c.c.; 75% solution) at 0° was added to the impure hydroperoxide (1·0 g.), acetone (10 c.c.) was added, and the salt was filtered off and washed with acetone. A solution of the salt in water (20 c.c.) was extracted with ether, and then acidified with 3N-acetic acid. Extraction with ether and distillation gave 1-phenylethyl hydroperoxide, b. p. 48°/0·01 mm., n_D^{20} 1·5250 (Found : C, 69·6; H, 7·8. Calc. for $C_8H_{10}O_2$: C, 69·8; H, 7·3%).

From a reaction with 98% formic acid (0·02 c.c.) as catalyst instead of sulphuric acid, a slightly yellow oil (2·0 g.) was recovered, containing 43% of 1-phenylethyl hydroperoxide; a similar experiment with no catalyst gave only 4% of the hydroperoxide. It was not possible to separate the hydroperoxide from unchanged alcohol by distillation.

(v) *Diphenylmethanol.* The alcohol (1·0 g.), as a saturated ethereal solution, was stirred for 6 hr. with hydrogen peroxide (10 c.c.) and concentrated sulphuric acid (0·02 c.c.). The ether extract of the diluted reaction mixture was washed with aqueous sodium hydrogen carbonate solution and dried (Na_2SO_4), yielding diphenylmethyl hydroperoxide (1·1 g.) as needles (from light petroleum) (0·60 g.), m. p. 50—52° (Found : C, 78·0; H, 6·2. Calc. for $C_{13}H_{12}O_2$: C, 78·0; H, 6·0%). Hock and Lang (*Ber.*, 1944, **77**, 257) reported m. p. 51° for the compound obtained by autoxidation of diphenylmethane.

Use of 98% formic acid (0·02 c.c.) instead of sulphuric acid gave material (9 g.) containing 30% of diphenylmethyl hydroperoxide, estimated volumetrically. In the absence of a catalyst a product (1·0 g.) containing 20% of the hydroperoxide was obtained.

(vi) 1 : 2 : 3 : 4-*Tetrahydro*-1-*naphthol.* A mixture of the alcohol (0·50 g.), hydrogen peroxide (10 c.c.), and 98% formic acid (0·02 c.c.) was stirred for 2 hr. and then set aside for 1·5 hr. The solid product was dried and crystallised from light petroleum, giving 1 : 2 : 3 : 4-tetrahydro-1-naphthyl hydroperoxide (0·20 g.), m. p. 54—56° undepressed on admixture with a sample obtained by the autoxidation of tetralin.

In the absence of any catalyst 0·70 g. (from 1 g. of alcohol) of recrystallised hydroperoxide, m. p. 56°, was obtained. This experiment was repeated with the optically active alcohol, $[\alpha]_D^{20}$ +30·0° (*l*, 2; *c*, 4·5 in $CHCl_3$), the inactive hydroperoxide being isolated.

(vii) sec.-*Butyl alcohol.* Reaction of the alcohol with hydrogen peroxide and concentrated sulphuric acid did not give a hydroperoxide.

(viii) 3 : 3-*Dimethylbutan*-2-*ol.* It was hoped that rearrangement of the carbon skeleton during reaction (Whitmore *et al.*, *J. Amer. Chem. Soc.*, 1933, **55**, 1107) with the consequent formation of the known 1 : 1 : 2-trimethylpropyl hydroperoxide (Criegee and Dietrich, *loc. cit.*) would afford evidence for the formation of a free carbonium ion in the transition state of reaction. However, from the sulphuric acid catalysed reaction, after 216 hr., including 46 hr.' stirring at room temperature, the alcohol (3·2 c.c. from 5 c.c.) was recovered, leaving only 0·085 g. of a residue, b. p. 54—54°/15 mm., which liberated iodine from potassium iodide. An attempt to prepare the *p*-nitrobenzoate of this residue (Criegee and Dietrich, *loc. cit.*) was unsuccessful.

Reaction between 85—90% *Hydrogen Peroxide and Carboxylic Esters.*—(i) 1 : 2 : 3 : 4-*Tetrahydro*-1-*naphthyl hydrogen phthalate.* From an initially homogeneous solution of the hydrogen phthalate (2·0 g.) in hydrogen peroxide (15 c.c.) containing sodium hydrogen carbonate (1·4 g., 2·5 mols.), an oil began to separate on the surface after 0·5 hr. After 22 hr., water (15 c.c.) was added; the oil was extracted with ether, the extract washed and dried (Na_2SO_4), and the solvent removed, yielding a solid (0·90 g.). Recrystallisation from light petroleum gave 1 : 2 : 3 : 4-tetrahydro-1-naphthyl hydroperoxide (0·50 g.), m. p. and mixed m. p. 56°. In a similar experiment, the optically active ester, $[\alpha]_D^{19}$ +11·1° (*l*, 2; *c*, 4·1 in $CHCl_3$), yielded the optically inactive hydroperoxide.

(ii) 1 : 2 : 3: 4-*Tetrahydro*-1-*naphthyl acetate.* After being stirred for 6 hr., a mixture of the acetate (1·0 g.), hydrogen peroxide (10 c.c.), and 98% formic acid (0·02 c.c.) was extracted with ether, the extract washed with sodium hydrogen carbonate solution and dried (Na_2SO_4), and the solvent removed. The reddish-yellow oil was extracted with boiling light petroleum, yielding 1 : 2 : 3 : 4-tetrahydro-1-naphthyl hydroperoxide (0·04 g.), m. p. 56°. The yield was low because of decomposition of the hydroperoxide by the formic and acetic acids.

(iii) *Diphenylmethyl hydrogen phthalate.* A water-cooled solution of the hydrogen phthalate (0·5 g.) in hydrogen peroxide (5 c.c.) containing sodium hydrogen carbonate (0·3 g., 2·5 mols.) was diluted with water after 48 hr.; an ethereal extract yielded diphenylmethyl hydroperoxide (0·15 g.), m. p. 51° (from light petroleum), undepressed on admixture with the hydroperoxide obtained from diphenylmethanol. After acidification of the aqueous residue with 50% hydrochloric acid, some unchanged ester (0·14 g.), m. p. 145—147°, was obtained.

(iv) 1-iso*Butyl*-1-*methylpropyl hydrogen phthalate.* After 16 hr., a solution of the hydrogen phthalate (kindly supplied by Drs. Kenyon and Wadden), m. p. 61—63° (1 g.), in hydrogen peroxide (5 c.c.) containing sodium hydrogen carbonate (0·76 g., 2·5 mols.) was diluted with water (10 c.c.) and extracted with ether. The washed and dried extract yielded 1-*iso*butyl-1-methylpropyl hydroperoxide (0·04 g.), identified as the hydrogen perphthalate (0·02 g.), m. p. and mixed m. p. 86—88°. By acidification of the aqueous residue from the reaction, some ester (0·64 g.), m. p. 60—62°, was recovered.

(v) 1-*Phenylethyl hydrogen phthalate.* Reaction of the hydrogen phthalate with hydrogen peroxide (10 c.c.) containing sodium hydrogen carbonate (1·5 g., 2·5 mols.) for 24 hr. gave no hydroperoxide, and 90% of the ester was recovered.

(vi) *Methyl hydrogen phthalate and* 2-*octyl hydrogen phthalate.* Solutions of the sodium salts of these half-esters are not stable in concentrated hydrogen peroxide. However, if the reaction mixtures were diluted with water when the final violent stage seemed imminent, the original hydrogen phthalates could be recovered in about 70% yield. No other reaction products could be isolated.

Reaction between Hydrogen Peroxide and sec.-*Butyl Sodium Sulphate.*—*sec.*-Butyl sodium sulphate was prepared from the alcohol, sulphamic acid, and pyridine (Burwell and Holmquist, *J. Amer. Chem. Soc.*, 1949, **71**, 1769). After 18 hr., no organic material could be obtained by ethereal extraction of a solution of the sulphate (0·5 g.) and sodium hydrogen carbonate (0·48 g.) in 85—90% hydrogen peroxide. Similarly no *sec.*-butyl hydroperoxide could be isolated, after 18 hr., from a mixture of the sulphate (8·8 g.), 85—90% hydrogen peroxide (6 c.c.), and aqueous potassium hydroxide (2·8 g. in 7·2 c.c. of water).

Reaction between 85—90% *Hydrogen Peroxide and Olefins.*—(i) iso*Pent*-2-*ene.* A mixture of the olefin (5 c.c.), hydrogen peroxide (5 c.c.), and concentrated sulphuric acid (0·02 c.c.) was stirred for 6 hr. and set aside for 16 hr. Water was then added and the product extracted with light petroleum, yielding *tert.*-amyl hydroperoxide (1·29 g.), b. p. 63—64°/37·5 mm., n_D^{20} 1·4158, from which was prepared the hydrogen perphthalate, m. p. and mixed m. p. 88—90° (decomp.) (Found : equiv., 252. Calc. for $C_{13}H_{16}O_5$: equiv., 252). The constitution of the hydroperoxide was further confirmed by its reduction, by aqueous sodium sulphite, to the corresponding alcohol, characterised as *tert.*-amyl *p*-nitrobenzoate, m. p. and mixed m. p. 83—84°.

(ii) *The olefin derived from* 3 : 5-*dimethylhexan*-3-*ol.* The olefin (5 c.c.; probably the unknown 3 : 5-dimethylhex-2-ene), obtained by dehydration of the alcohol, was stirred for 5 hr. with hydrogen peroxide (5 c.c.) and concentrated sulphuric acid (0·05 c.c.). The organic layer yielded 1-*iso*butyl-1-methylpropyl hydroperoxide (0·35 g.), b. p. 43°/0·1 mm., n_D^{25} 1·4333, from which was prepared the hydrogen perphthalate, m. p. and mixed m. p. 85—87° (Found : equiv., 296. Calc. for $C_{16}H_{22}O_5$: equiv., 294). A viscous residue (3·8 g.), b. p. >60°/0·1 mm., similar to that obtained in the preparation of the hydroperoxide from the alcohol and giving a strongly positive peroxide reaction with acidified potassium iodide–starch paper, was also isolated. A longer reaction period (19 hr.) resulted in the formation of only this high-boiling residue, which is probably the product of acid decomposition of the hydroperoxide. An attempted larger-scale preparation (10 c.c. of olefin) resulted in violent decomposition after 4 hr.

(iii) cyclo*Hexene.* Only the olefin was recovered from the reaction of *cyclo*hexene with hydrogen peroxide and concentrated sulphuric acid.

The infra-red absorption spectra of some of these peroxides, determined by Dr. G. J. Minkoff, wll be published elsewhere.

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