Organic Peroxides. Part III. The Preparation of Alkyl Hydroperoxides and Dialkyl Peroxides. Characteristic Derivatives of Alkyl Hydroperoxides.*

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The preparation of alkyl hydroperoxides by the reaction between 90% hydrogen peroxide and the carbonium ions obtained by the unimolecular alkyl–oxygen heterolysis of alcohols or carboxylic esters, or by the protonation of olefins (Part I *), has been extended to several new alkyl hydroperoxides. In analogous preparations of dialkyl peroxides, carbonium ions react with an alkyl hydroperoxide; the alkylation of alkyl hydroperoxides with xanthhydrol or triphenylmethanol produces crystalline derivatives suitable for the characterisation of the hydroperoxides.

Preparation of Alkyl Hydroperoxides.—We have shown (*Nature*, 1952, **170**, 668; *J.*, 1952, 3300; Part I,* and unpublished work on isotopically labelled compounds) that alkyl hydroperoxides may be prepared by nucleophilic attack of concentrated hydrogen peroxide on carbonium ions ($R^+ + HO{\cdot}OH \longrightarrow RO{\cdot}OH + H^+$) which may be generated by the unimolecular alkyl–oxygen heterolysis of alcohols or of carboxylic esters, or by the protonation of olefins. These reactions have now been extended to the preparation of a number of new alkyl hydroperoxides.

Good yields of 1-ethyl-1-methylbutyl, 4-methoxydiphenylmethyl, 4-phenyldiphenylmethyl, 1-methyl-1-phenylpropyl, and xanthhydryl hydroperoxide were obtained from the corresponding alcohols and 90% hydrogen peroxide. The conclusions reached in Part I * have been confirmed in that the reactivity of the various alcohols, as determined by the weakest acid which will bring about the reaction, is again parallel to their known tendency to undergo unimolecular alkyl–oxygen heterolysis (Kenyon and his co-workers, *J.*, 1942—54). Thus in the extremes, xanthhydrol, which is very reactive by such a mechanism (Balfe, Kenyon, and Thain, *J.*, 1952, 790), reacts with 90% hydrogen peroxide in homogeneous ethereal solution, and even with neutral 30% aqueous hydrogen peroxide, whereas benzyl alcohol was recovered after treatment with 90% hydrogen peroxide and concentrated sulphuric acid.

1-Methyl-1-phenylpropyl hydroperoxide has also been obtained by the solvolysis of 1-methyl-1-phenylpropyl hydrogen phthalate in 90% hydrogen peroxide containing an excess of sodium hydrogen carbonate, and 1-ethyl-1-methylbutyl hydroperoxide by the addition of hydrogen peroxide to the olefin derived from 3-methylhexan-3-ol (probably a mixture of 3-methylhex-2- and -3-ene).

Factors influencing Alkyl–Oxygen Heterolysis of Alcohols in Hydrogen Peroxide.—The high reactivity of certain alcohols towards hydrogen peroxide is noteworthy, and has been further investigated. Whereas 1 : 2 : 3 : 4-tetrahydro-1-naphthol (Part I) and xanthhydrol react readily with 90% hydrogen peroxide in the absence of added acid, this reactivity is completely suppressed by the addition of sodium hydrogen carbonate to the solution. Xanthhydrol reacts even with neutral 30% hydrogen peroxide, but 1 : 2 : 3 : 4-tetrahydro-1-naphthol reacts with this reagent only in the presence of sulphuric acid.

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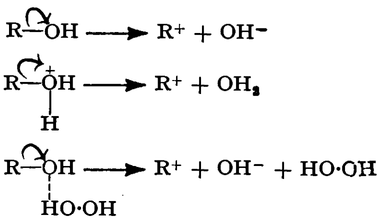
* Part I and II, *J.*, 1953, 1541, 1808.

To account for this unimolecular alkyl–oxygen heterolysis of alcohols in ostensibly neutral hydrogen peroxide, the following mechanisms may be considered :



(1) $R{-}OH \longrightarrow R^+ + OH^-$

(2) $R{-}\underset{H}{\overset{+}{O}}H \longrightarrow R^+ + OH_2$

(3) $R{-}\underset{HO\cdot OH}{O}H \longrightarrow R^+ + OH^- + HO\cdot OH$

The first, involving alkyl–oxygen heterolysis in the absence of catalysis (except for the usual solvation) is rather improbable in view of the strong nucleophilic power of the HO^- anion for a carbonium ion, and no previous examples appear to have been reported.

The assumption implicit in the second mechanism, that hydrogen peroxide is of itself * an acid strong enough to protonate the basic OH group in 1 : 2 : 3 : 4-tetrahydro-1-naphthol or xanthhydrol, and thus catalyse alkyl–oxygen heterolysis may well be true of 90% hydrogen peroxide, but seems less likely for dilute aqueous hydrogen peroxide. Mitchell and Wynne-Jones have shown (*Discuss. Faraday Soc.*, 1953, **15**, 161) that the acidity of pure hydrogen peroxide is about 10^9 times greater than that of water; this acidity is emphasised by the fact that we find that 90% hydrogen peroxide reacts vigorously with sodium hydrogen carbonate with the evolution of carbon dioxide without loss of oxygen. Aqueous 50% hydrogen peroxide reacts very slowly, and 30% hydrogen peroxide is unreactive.†

The weakening of the alkyl–oxygen bond by the formation of a hydrogen bond between an H_2O_2 molecule and the oxygen atom of the alcoholic group (eqn. **3**) would be analogous to that postulated (Cowdrey, Hughes, Ingold, Masterman, and Scott, *J.*, 1937, 1266) for the replacement of OH by halogen with halogen hydracids. In view of the known ability of hydrogen peroxide to form strong hydrogen bonds (Scatchard, Kavanagh, and Ticknor, *J. Amer. Chem. Soc.*, 1952, **74**, 3715) this seems the most probable cause of the reactivity of xanthhydrol towards neutral 30% hydrogen peroxide.

Preparation of Dialkyl Peroxides.—By analogy with our methods of preparation of alkyl hydroperoxides, reactions in which carbonium ions are generated in media containing alkyl hydroperoxides might be expected to yield dialkyl peroxides ($R^+ + R'O\cdot OH \longrightarrow RO\cdot OR' + H^+$). This has been confirmed, and examples of such reactions have been established in which the carbonium ion is again produced by alkyl–oxygen heterolysis of alcohols and of esters, or by protonation of olefins.

Xanthhydrol and triphenylmethanol in acetic and acetic–sulphuric acid solution, respectively, react readily with alkyl hydroperoxides to form the corresponding crystalline alkyl xanthhydryl or alkyl triphenylmethyl peroxides in good yields (see Table). Attempts to prepare di-*p*-methoxyphenylmethyl hydroperoxide from the alcohol and hydrogen peroxide gave only bis(di-*p*-methoxyphenylmethyl) peroxide. Apparently the alkyl hydroperoxide which is first formed is then alkylated by a second molecule of the alcohol which very readily undergoes alkyl–oxygen heterolysis (Balfe, Kenyon, and Thain, *J.*, 1951, 386; 1952, 790).

1-Methyl-1-phenylpropyl hydrogen phthalate in acetic–sulphuric acid readily reacts with *tert.*-butyl hydroperoxide, to form *tert.*-butyl 1-methyl-1-phenylpropyl peroxide, identical with the product of the analogous reaction of 2-phenylbutan-2-ol. The reaction of alkyl hydroperoxides with olefins has been exemplified by the preparation of *tert.*-amyl *tert.*-butyl peroxide from 2-methylbut-2-ene and *tert.*-butyl hydroperoxide, under similar acid conditions.

Various crystalline esters are available for the characterisation of saturated *tert.*-alkyl hydroperoxides; Criegee and Dietrich (*Annalen*, 1948, **560**, 135) have prepared the *p*-nitro-

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* The hydrogen peroxide used contained no acidic stabiliser.

† The medium for the solvolysis of hydrogen phthalic esters, which we have described (Part I) as 90% hydrogen peroxide containing sodium hydrogen carbonate, thus in fact contains very few hydrogen carbonate anions.

perbenzoates, and we have described the 1-hydrogen 1-monoperphthalates (Part I) and the percarbamates (Part II). None of these derivatives, however, can readily be prepared from the 1-arylalkyl hydroperoxides. For example, 1 : 2 : 3 : 4-tetrahydro-1-naphthyl hydroperoxide with phthalic anhydride in pyridine gives only 1 : 2 : 3 : 4-tetrahydro-1-oxonaphthalene (A. M. White, Thesis, London, 1953). The xanthhydryl and triphenylmethyl derivatives described here should therefore be valuable for the isolation and characterisation of the hydroperoxides of low molecular weight present in the products of the autoxidation or combustion of hydrocarbons.

EXPERIMENTAL

Light petroleum refers to the fraction with b. p. 40—60°. Unless otherwise stated, solutions in organic solvents were dried over anhydrous sodium sulphate. Unstabilised 85—90% hydrogen peroxide and 60% *tert.*-butyl hydroperoxide were supplied by Messrs. Laporte Chemicals Ltd., Luton.

Explosion Hazards.—In all reactions involving organic peroxides, precautions were taken to minimise the effect of a possible explosion. No such explosion was encountered, and none of the peroxides described appears to be liable to explode in presence of traces of acid or dust, or on scratching, at temperatures below about 100°. It is recommended, however, that the reactions should not be carried out on a large scale until detonation tests on the reaction mixtures and products have indicated more clearly the hazards involved.

Purification of Commercial 60% tert.-*Butyl Hydroperoxide.*—The commercial material contains some free hydrogen peroxide which is best removed before distillation is attempted. The 60% *tert.*-butyl hydroperoxide is diluted with an equal volume of light petroleum, washed three times with water, and then thoroughly dried. Distillation from a bath at 65° gives a first fraction (b. p. 35—45°/85 mm.) consisting mainly of *tert.*-butyl peroxide, after which the *tert.*-butyl hydroperoxide distills, b. p. 36°/16 mm. The yield is about 40%.

Reaction between 85—90% *Hydrogen Peroxide and Alcohols.*—(i) 3-*Methylhexan*-3-*ol.* A mixture of the alcohol (3·4 g.; b. p. 52—54°/20 mm.), 90% hydrogen peroxide (5 c.c.), and concentrated sulphuric acid (0·04 c.c.) was stirred for 6 hr. at room temperature; water was then added, the solution extracted with ether, and the ethereal extract washed and dried. Two distillations yielded 1-*ethyl*-1-*methylbutyl hydroperoxide* (3·0 g.), b. p. 34°/0·1 mm., n_D^{20} 1·4300 (Found: C, 63·7; H, 12·0. $C_7H_{16}O_2$ requires C, 63·7; H, 12·2%). By the method described in Part I (*loc. cit.*), from the hydroperoxide (0·5 g.), phthalic anhydride (0·6 g.), and pyridine (0·45 g.), after 2 days at room temperature, 1-(1-*ethyl*-1-*methylbutyl*) *hydrogen* 1-*monoperphthalate* (0·82 g.) was obtained which, recrystallised from ether–light petroleum, showed m. p. 90—92° (Found: C, 63·8; H, 7·0%; equiv., 279. $C_{15}H_{20}O_5$ requires C, 64·2; H, 7·2%; equiv., 280).

(ii) 4-*Methoxydiphenylmethanol.* The alcohol (2·0 g.) in ether (10 c.c.) was stirred for 6 hr. with 90% hydrogen peroxide (10 c.c.) and 98% formic acid (0·02 c.c.). An ethereal extract of the diluted mixture yielded 4-*methoxydiphenylmethyl hydroperoxide* as white needles (from light petroleum), m. p. 50—51° (Found: C, 72·4; H, 6·6. $C_{14}H_{14}O_3$ requires C, 73·1; H, 6·1%). From a similar reaction with concentrated sulphuric acid as the catalyst, only the products of acid decomposition, *p*-methoxyphenol (0·9 g., m. p. and mixed m. p. 52·5—53°) and benzoic acid (0·04 g.; m. p. and mixed m. p. 120·5°) were isolated.

(iii) 4-*Phenyldiphenylmethanol.* After 6 hours' stirring, a mixture of the alcohol (1·0 g.) in ether (10 c.c.), hydrogen peroxide (10 c.c.), and concentrated sulphuric acid (0·02 c.c.) was diluted with water, and extracted with ether, yielding a solid (1·0 g.) which was recrystallised from benzene, giving 4-*phenyldiphenylmethyl hydroperoxide* as leaflets, m. p. 162·5—163° (Found: C, 83·4; H, 6·0. $C_{19}H_{16}O_2$ requires C, 82·6; H, 5·8%).

(iv) 2-*Phenylbutan*-2-*ol.* The alcohol (5·0 c.c.), 90% hydrogen peroxide (5 c.c.), and concentrated sulphuric acid (0·05 c.c.) were stirred at room temperature for 6 hr. Water (10 c.c.) was then added, and the upper organic layer extracted with light petroleum, washed with water, and dried. Distillation yielded 1-methyl-1-phenylpropyl hydroperoxide, b. p. 60°/0·01 mm., n_D^{20} 1·5230.

(v) *Xanthhydrol.* The alcohol (2·0 g.) in ether (10 c.c.) was stirred for 4 hr. with 90% hydrogen peroxide (10 c.c.). *Xanthhydryl hydroperoxide* (1·77 g.) was precipitated by the addition of light petroleum to the ethereal extract of the diluted mixture, and recrystallised from ether–light petroleum mixture as colourless prisms, m. p. 123—124° (Found: C, 73·0; H, 4·6. $C_{13}H_{10}O_3$ requires C, 72·9; H, 4·6%). The same product was obtained with aqueous 30% hydrogen peroxide, and with a homogeneous solution of 90% hydrogen peroxide (5 c.c.) in ether (about 30 c.c.).

(vi) *Di*-p-*methoxyphenylmethanol.* After 4 hours' stirring, the alcohol (1·0 g.) in ether (10 c.c.), hydrogen peroxide (10 c.c.), and 98% formic acid (0·02 c.c.) yielded *bis*(*di*-p-*methoxyphenylmethyl*) *peroxide* (0·60 g.) as white needles (from ether–light petroleum mixture), m. p. 128·5—129·5° (Found : C, 74·5; H, 6·3. $C_{30}H_{30}O_6$ requires C, 74·1; H, 6·2%).

Benzyl alcohol was recovered unchanged from reaction mixtures containing sulphuric acid or formic acid as catalysts. 4-Methyldiphenylmethanol reacted in the presence of sulphuric acid, but not formic acid; the hydroperoxide was an unstable oil, which did not solidify.

Reaction between 85—90% *Hydrogen Peroxide and* 1-*Methyl*-1-*phenylpropyl Hydrogen Phthalate.*—From an initially homogeneous solution of the hydrogen phthalate (2·0 g., 1·0 mol.) in hydrogen peroxide (10 c.c.) containing sodium hydrogen carbonate (1·5 g., 2·6 mols.) at 0°, an oil separated on the surface after 2 hr. After a further 20 hr., water (25 c.c.) was added; a light petroleum extract yielded an oil (0·59 g.) which on distillation gave 1-methyl-1-phenylpropyl hydroperoxide, b. p. 72—73°/0·02 mm., n_D^{20} 1·5224 (Found : C, 72·3; H, 8·8. Calc. for $C_{10}H_{14}O_2$: C, 72·3; H, 8·4%); Ivanov, Savinova, and Zhakhovskaya (*Doklady Acad. Nauk S.S.S.R.*, 1948, **59**, 905) report b. p. 48—49°/0·002 mm., n_D^{20} 1·5208, and Hawkins (*J.*, 1949, 2076) reports b. p. 58—58·5°/0·01 mm., n_D^{20} 1·5206.

Reaction between 85—90% *Hydrogen Peroxide and* 3-*Methylhexenes.*—The olefin, b. p. 84—96°, probably a mixture of 3-methylhex-3- and -2-ene, was obtained by heating 3-methylhexan-3-ol under reflux with 1% of iodine (Edgar, Calingaert, and Marker, *J. Amer. Chem. Soc.*, 1929, **51**, 1486). This olefin (5 c.c., 3·7 g.) was stirred with hydrogen peroxide (5 c.c.) and concentrated sulphuric acid (0·02 c.c.) in a sealed flask to prevent evaporation of the olefin. After 6 hr., water was added (25 c.c.). The ethereal extract yielded the crude hydroperoxide (2·6 g.) which was distilled, giving 1-ethyl-1-methylbutyl hydroperoxide (1·4 g.), b. p. 36—37°/0·2 mm., n_D^{20} 1·4304. From this, the hydrogen perphthalate was prepared, having m. p. and mixed m. p. 90—92°.

Reaction between Alkyl Hydroperoxides and Alcohols.—The alkyl hydroperoxides used were analysed specimens prepared as described above, or as in Part I (*loc. cit.*).

			Found (%)			Required (%)	
Second group	M. p.	Solvent	C	H	Formula	C	H
Alkyl xanthhydryl peroxides.							
Me_3C	69—71°	Aq. EtOH	75·7	7·0	$C_{17}H_{18}O_3$	75·6	6·7
$EtMe_2C$	41—42	,,	75·7	7·0	$C_{18}H_{20}O_3$	76·1	7·0
PrEtMeC	liquid	—	—	—	—	—	—
PhMeCH	84—86	Pet, 1	79·5	5·9	$C_{21}H_{18}O_3$	79·2	5·7
Ph_2CH	117	Pet, 2	81·6	5·4	$C_{26}H_{20}O_3$	82·1	5·3
α-Tetralyl	125	$COMe_2$	79·9	6·1	$C_{23}H_{20}O_3$	80·2	5·9
$PhMe_2C$	97—98	Pet, 1	79·2	6·2	$C_{22}H_{20}O_3$	79·5	5·9
PhEtMeC	82—83	EtOH	79·6	6·4	$C_{23}H_{22}O_3$	79·8	6·4
Xanthhydryl	152—153	EtOH	79·3	4·7	$C_{26}H_{18}O_4$	79·2	4·6 [a]
Alkyl triphenylmethyl peroxides.							
Me_3C	72·5—73	MeOH	83·1	7·9	$C_{23}H_{24}O_2$	83·1	7·3 [b]
$EtMe_2C$	Liquid	—	—	—	—	—	—
PrEtMeC	50—52	Aq. EtOH	83·4	8·0	$C_{26}H_{30}O_2$	83·4	8·1
PhMeCH	85—86	EtOH	84·6	6·4	$C_{27}H_{24}O_2$	85·2	6·4
Ph_2CH	86—88	Pet, 2	86·5	5·8	$C_{32}H_{26}O_2$	86·8	5·9 [c]
α-Tetralyl	91—92	EtOH	85·3	6·4	$C_{29}H_{26}O_2$	85·7	6·4 [d]
$PhMe_2C$	168—169	[e]	85·3	5·9	$C_{28}H_{26}O_2$	85·3	6·6

Pet = light petroleum, 1 = b. p. 40—60°, 2 = b. p. 100—120°.

[a] Xanthhydryl peroxide may also be obtained by warming xanthhydryl hydroperoxide in acetic acid (see succeeding paper). [b] Kharasch *et al.*, *J. Org. Chem.*, 1951, **16**, 1465, report m. p. 72—73°. [c] Bachman and Wiselogle, *ibid.*, 1937, **1**, 354, report m. p. 93—94° for this compound obtained by the autoxidation of pentaphenylethane. [d] Kharasch and Burt, *ibid.*, 1951, **16**, 150, report m. p. 96—97°. [e] The solid, precipitated from solution during the reaction, was insoluble in common organic solvents, and was purified by washing with a large volume of hot ethanol.

(i) *Reaction between* 2-*phenylbutan*-2-*ol and* tert.-*butyl hydroperoxide.* A solution of the alcohol (7·5 g.) and *tert.*-butyl hydroperoxide (4·5 g.) in glacial acetic acid (15 c.c.) containing concentrated sulphuric acid (0·5 g.) became opalescent after 0·5 hr. and a lower liquid layer separated. After 5 hours' stirring, water (45 c.c.) was added, and the product extracted with ether, washed with saturated aqueous potassium carbonate till neutral, and dried (K_2CO_3). Distillation yielded tert.-*butyl* 1-*methyl*-1-*phenylpropyl peroxide* (7·17 g.), b. p. 50—51°/0·4 mm., n_D^{25} 1·4786, d_4^{25} 0·932 (Found : C, 76·0; H, 10·1. $C_{14}H_{22}O_2$ requires C, 75·6; H, 10·0%).

(ii) *Preparation of xanthhydryl derivatives of alkyl hydroperoxides.* The alkyl hydroperoxide

(0·5 g.), dissolved in chloroform if a solid, was added to a solution of xanthhydrol (1 mol.) in glacial acetic acid (10 c.c.). After 0·5—1 hr. at room temperature (with stirring if solid had separated), the mixture was poured on crushed ice, and the precipitated *alkyl xanthhydryl peroxide* was recrystallised. Yields of recrystallised material were usually better than 60%. Details of solvents, m. p., and analyses are given in the Table.

(iii) *Preparation of triphenylmethyl derivatives of alkyl hydroperoxides.* The alkyl hydroperoxide (0·5 g.), dissolved in chloroform if a solid, was added to a solution of triphenylmethanol (1 mol.) in glacial acetic acid (20 c.c.) containing concentrated sulphuric acid (0·05 c.c.). After 2 hr. at room temperature, the mixture was poured on ice, and the *alkyl triphenylmethyl peroxide* which separated was recrystallised. Yields again were usually better than 60%. Details are given in the Table.

Reaction between tert.*-Butyl Hydroperoxide and 2-Methylbut-2-ene.*—Concentrated sulphuric acid (1·0 c.c.) was added slowly to a solution of 2-methylbut-2-ene (4·0 g.) and *tert.*-butyl hydroperoxide (5·0 g.) in acetic acid (30 c.c.), cooled in water. After 18 hr. at room temperature, the mixture was poured into water; the organic layer was washed with dilute sodium hydroxide solution and with saturated aqueous potassium carbonate and dried (K_2CO_3), yielding *tert.*-amyl *tert.*-butyl peroxide (6·0 g.), b. p. 125—127° (slight decomp.), n_D^{20} 1·3980 (Found: C, 67·3; H, 12·5. Calc. for $C_9H_{20}O_2$: C, 67·5; H, 12·5%). Rust, Dickey, and Bell (U.S.P. 2,403,758; B.P. 591,543) prepared this compound from *tert.*-butyl hydroperoxide and *tert.*-amyl alcohol, and report the b. p. of an aqueous azeotrope as 91—92°, n_D^{20} 1·4000.

Reaction between 1-Methyl-1-phenylpropyl Hydrogen Phthalate and tert.*-Butyl Hydroperoxide.*—Concentrated sulphuric acid (0·1 c.c.) in acetic acid (1·0 c.c.) was added to the hydrogen phthalate (2·31 g.) and *tert.*-butyl hydroperoxide (0·7 g.) in glacial acetic acid (20 c.c.). Scratching caused immediate precipitation of phthalic aicd (1·00 g.; m. p. 192—194°). After 10 min., the filtrate was diluted with water, and the precipitated oil extracted with ether, washed with saturated aqueous potassium carbonate till neutral, and dried (K_2CO_3). Distillation yielded *tert.*-butyl 1-methyl-1-phenylpropyl peroxide (0·55 g.), n_D^{25} 1·4786 (Found: C, 75·9; H, 9·9. Calc. for $C_{14}H_{22}O_2$: C, 75·6; H, 10·0%).

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