Organic Peroxides. Part IV. Alkyl–Oxygen Heterolysis in Organic Peroxides.*

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Alkyl hydroperoxides and dialkyl peroxides undergo unimolecular alkyl–oxygen heterolysis to form carbonium ions, which are detected by their characteristic reactions with suitable nucleophilic reagents.

MUCH of the interest in organic peroxides arises from the multiplicity of types of bond fission which such molecules undergo. Apart from the familiar oxygen–oxygen homolysis (Leffler, *Chem. Reviews*, 1949, **45**, 385) and the oxygen–hydrogen homolysis more recently reported (Campbell and Coppinger, *J. Amer. Chem. Soc.*, 1952, **74**, 1469; Kharasch, Pauson, and Nudenberg, *J. Org. Chem.*, 1953, **18**, 322), two types of bond heterolysis are well established. Hydrogen–oxygen heterolysis ($\mathrm{RO{\cdot}\overset{\curvearrowleft}{O{-}H}}$) in alkyl hydroperoxides occurs in their nucleophilic reactions, *e.g.*, formation of dialkyl peroxides by alkylation

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* Part III, preceding paper.

with alcohols and olefins (Part III *), esterification (Parts I and II, *J.*, 1953, 1541, 1808), carbonyl addition (Rieche, *Ber.*, 1930, **63**, 2642), and epoxide addition (Barusch and Payne, *J. Amer. Chem. Soc.*, 1953, **75**, 1987). Of more recent recognition is the oxygen–oxygen heterolysis of peroxides ($\mathrm{RO{-}\overset{\curvearrowleft}{O}{\cdot}R'}$; Leffler, *loc. cit.*) which has been described in the reactions of peracids (Swern, *J. Amer. Chem. Soc.*, 1947, **69**, 1692), in the decomposition of peresters (Criegee, *Annalen*, 1948, **560**, 127), in the acid-catalysed (Kharasch, Fono, and Nudenberg, *J. Org. Chem.*, 1950, **15**, 748) and base-catalysed (Kornblum and de la Mare, *J. Amer. Chem. Soc.*, 1951, **73**, 880) decomposition of alkyl hydroperoxides and dialkyl peroxides, and in the acid-catalysed rearrangements of diacyl peroxides (Leffler, *ibid.*, 1950, **72**, 67). This heterolysis is usually accompanied, in the RO group, by loss of a proton from the α-position, or by migration of an α-alkyl or α-aryl group on to the oxygen atom, to form ultimately a carbonyl compound or its derivative (Kharasch, Fono, Nudenberg, and Poshkus, *J. Org. Chem.*, 1950, **15**, 775).

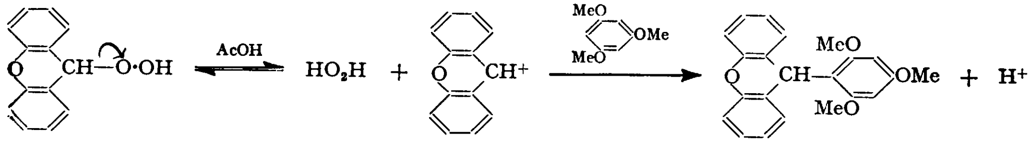
A third possible mode of bond heterolysis in alkyl hydroperoxides and dialkyl peroxides, that of alkyl–oxygen heterolysis probably by a unimolecular mechanism, *i.e.*, $\mathrm{RO{\cdot}OR'} \overset{H^+}{\rightleftharpoons} \mathrm{R{-}\underset{H}{\overset{\curvearrowleft +}{O}}{\cdot}OR'} \rightleftharpoons \mathrm{R'O{\cdot}OH} + \mathrm{R^+} \xrightarrow{Y} \mathrm{RY}$, is now described.

The affinity of an oxygen atom for the electrons of either the alkyl–oxygen or the oxygen–oxygen bond will normally be small, but bond heterolysis in both of these senses will be susceptible to acid catalysis by the increase of the electron affinity of the oxygen atom by protonation. If the electron-releasing power of the group R is small, oxygen–oxygen heterolysis usually occurs, as described above. However, if group R strongly releases electrons, then unimolecular alkyl–oxygen heterolysis may occur with comparable or greater readiness, leading to the formation of carbonium ions; thus it is in compounds such as the xanthhydryl, triphenylmethyl, and di-*p*-methoxyphenylmethyl peroxides, under acid conditions, that unimolecular alkyl–oxygen fission may be expected (Parts I and III, *locc. cit.*). The presence of the carbonium ions in solution may be detected by their characteristic reactions with suitable nucleophilic reagents, as demonstrated by Kenyon and his co-workers (*J.*, 1942—54) for alcohols and esters.

The simplest reaction of this type which we have encountered is the disproportionation reaction of xanthhydryl hydroperoxide in acetic acid solution. It occurs rapidly on warming, more slowly at room temperature, to give xanthhydryl peroxide and hydrogen peroxide. One molecule of the hydroperoxide, by undergoing unimolecular alkyl–oxygen fission (as to the reactivity of xanthhydrol by a similar mechanism, see Balfe, Kenyon, and Thain, *J.*, 1952, 790, and Part III, *loc. cit.*), provides a carbonium ion which alkylates a second alkyl hydroperoxide molecule, *i.e.*, $\mathrm{X{-}\overset{\curvearrowleft}{O}{\cdot}OH} \overset{H^+}{\rightleftharpoons} \mathrm{HO{\cdot}OH} + \mathrm{X^+} \xrightarrow{\mathrm{XO{\cdot}OH}} \mathrm{XO{\cdot}OX} + \mathrm{H^+}$ (X = xanthhydryl). This disproportionation reaction is a general characteristic of molecules which contain a nucleophilic centre and can undergo unimolecular alkyl–oxygen heterolysis (*e.g.*, alcohols, alkyl hydrogen phthalates, and alkyl hydrogen sulphates).

The presence of intermediate carbonium ions has also been demonstrated by their reactions with the following added nucleophilic reagents: (*a*) aromatic compounds reactive to electrophilic substituting agents, (*b*) sodium toluene-*p*-sulphinate, (*c*) urea, (*d*) ethyl acetoacetate, and (*e*) acetone. In all cases the experiments with the peroxide have been preceded by an experiment with the corresponding alcohol, and the identity of the products obtained by alkyl–oxygen heterolysis from the two reactions has been confirmed. For the characterisation of carbonium ions by the use of aromatic compounds we have employed 1 : 3 : 5-trimethoxy- and 1 : 3 : 5-triethoxy-benzene. These are readily alkylated by xanthhydrol or di-*p*-methoxyphenylmethanol in acetic acid, and by 1 : 2 : 3 : 4-tetrahydro-1-naphthol in acetic–sulphuric acid, to give the corresponding alkylated trialkoxybenzene in good yield. The reactions of alcohols with reagents (*b*), (*c*), and (*d*) have been described by Kenyon *et al.* (*loc. cit.*), except the preparation of 1-methyl-1-phenylpropyl *p*-tolyl sulphone, which is now reported.

Xanthhydryl hydroperoxide, xanthhydryl peroxide, bis(di-*p*-methoxyphenylmethyl) peroxide, and 1 : 2 : 3 : 4-tetrahydro-1-naphthyl hydroperoxide react with the *s*-trialkoxybenzenes under the same conditions as the corresponding alcohols, to yield the respective alkylated aromatic compounds, *e.g.*:



From the reactions of the last two peroxides, some of the products of oxygen–oxygen heterolysis were also isolated.

Xanthhydryl peroxide and sodium toluene-*p*-sulphinate in acetic acid give *p*-tolyl xanthhydryl sulphone in good yield. The same product was obtained from the unsymmetrical peroxides, 1 : 2 : 3 : 4-tetrahydro-1-naphthyl xanthhydryl peroxide, and *tert.*-butyl xanthhydryl peroxide, as would be expected from the known relative tendencies of the *tert.*-butyl, 1 : 2 : 3 : 4-tetrahydro-1-naphthyl, and xanthhydryl groups to undergo unimolecular alkyl–oxygen heterolysis (Parts I and III). After reaction of *tert.*-butyl xanthhydryl peroxide, the liberated *tert.*-butyl hydroperoxide was isolated and characterised as 1-*tert.*-butyl hydrogen 1-monoperphthalate. Similarly, *tert.*-butyl triphenylmethyl peroxide, bis(di-*p*-methoxyphenylmethyl) peroxide, and *tert.*-butyl 1-methyl-1-phenylpropyl peroxide react with sodium toluene-*p*-sulphinate in acetic–sulphuric acid, to form *p*-tolyl triphenylmethyl sulphone, di-*p*-methoxyphenylmethyl *p*-tolyl sulphone, and 1-methyl-1-phenylpropyl *p*-tolyl sulphone, respectively. 1 : 2 : 3 : 4-Tetrahydro-1-naphthyl hydroperoxide and 1-methyl-1-phenylpropyl hydroperoxide do not form sulphones, but undergo the alternative reaction of reduction to the corresponding alcohols. The mechanism of the reduction is unknown, but from the fact that no sulphone could be isolated, it appears improbable that a free carbonium ion is involved at any stage in the reaction.

Again, xanthhydryl peroxide in acetic acid readily reacts with urea, and with ethyl acetoacetate, to form *s*-dixanthhydrylurea, and ethyl xanthhydrylacetoacetate, respectively, in good yield. Similarly *tert.*-butyl xanthhydryl peroxide and *tert.*-amyl xanthhydryl peroxide react with acetone under acid conditions to form xanthhydrylacetone.

The possibility merits consideration that these reactions might involve alkyl–oxygen homolysis rather than heterolysis. The following are the principal reasons why this alternative has been rejected. (*a*) All the reactions are susceptible to acid catalysis, which is interpretable on the basis of a heterolytic (see above) but hardly a homolytic mechanism. (*b*) The reaction conditions and products are always analogous to those of the corresponding alcohols. The reactivity of the latter follows the order predicted from a knowledge of the structural factors affecting the rates of S_N1 reactions (Part I); if such reactions involved free alkyl radicals it would be expected that, for example, a solution of triphenylmethanol in acetic–sulphuric acid in the presence of air would yield triphenylmethyl peroxide. (*c*) The products arising from alkyl–oxygen homolysis would probably be different from those obtained. Thus triphenylmethyl radicals do not undergo the reactions of strong electrophilic reagents; at room temperature they do not react with acetone, and form only loose molecular complexes with higher ketones, nitriles, aromatic compounds, and similar nucleophilic reagents (Gomberg, *J. Amer. Chem. Soc.*, 1914, **36**, 1144). It therefore appears safe to assume that the reactions described here proceed by alkyl–oxygen heterolysis.

Reactions of the type described above provide a method for the isolation and purification of impure alkyl hydroperoxides *via* the preparation (Part III), fractional crystallisation, and subsequent alkyl–oxygen heterolysis of their xanthhydryl or triphenylmethyl derivatives. These reactions may also provide a new route for the preparation of hydrogen peroxide by alkyl–oxygen heterolysis of alkyl hydroperoxides obtained from the autoxidation of hydrocarbons, and for the preparation of alkyl hydroperoxides by the alkylation of a reactive alkyl hydroperoxide, followed by the removal of the reactive alkyl group by alkyl–oxygen heterolysis.

EXPERIMENTAL

Alkyl hydroperoxides and peroxides were prepared as described in Parts I and III (*locc. cit.*).

Reaction between Alcohols and 1 : 3 : 5-*Trimethoxy- and* 1 : 3 : 5-*Triethoxy-benzene.*—(i) *Xanthhydrol.* A mixture of xanthhydrol (1·0 g.) in glacial acetic acid (10 c.c.) and 1 : 3 : 5-trimethoxybenzene (1·0 g.) also in acetic acid (10 c.c.), after 20 hr. at room temperature, was poured over crushed ice, and the precipitate was recrystallised from butanol, yielding 1 : 3 : 5-*trimethoxy-2-xanthhydrylbenzene* (1·20 g.) as colourless rhombs, m. p. 159—160° (Found : C, 75·8; H, 5·7. $C_{22}H_{20}O_4$ requires C, 75·9; H, 5·8%). 1 : 3 : 5-*Triethoxy-2-xanthhydrylbenzene*, prepared similarly, was obtained as needles (from butanol), m. p. 157·5—158·5° (Found : C, 76·5; H, 6·8. $C_{25}H_{26}O_4$ requires C, 76·9; H, 6·7%).

(ii) *Di-*p*-methoxyphenylmethanol.* After 20 hr., a mixture of di-*p*-methoxyphenylmethanol (0·5 g.) and 1 : 3 : 5-trimethoxybenzene (0·35 g.) in acetic acid (18 c.c.) was poured over ice, yielding 2 : 4 : 6 : 4′ : 4″-*pentamethoxytriphenylmethane* (from propanol; 0·74 g.) as needles, m. p. 102—103° (Found : C, 73·2; H, 6·7. $C_{24}H_{26}O_5$ requires C, 73·1; H, 6·6%). Similarly, from the alcohol (0·5 g.) and 1 : 3 : 5-triethoxybenzene (0·43 g.), 2 : 4 : 6-*triethoxy-4′* : *4″-dimethoxytriphenylmethane* (0·77 g.) was obtained as needles (from propanol), m. p. 108—109° (Found : C, 73·9; H, 7·7. $C_{27}H_{32}O_5$ requires C, 74·3; H, 7·3%).

(iii) 1 : 2 : 3 : 4-*Tetrahydro*-1-*naphthol.* A mixture of the alcohol (0·5 g.) and 1 : 3 : 5-trimethoxybenzene (0·57 g.) in acetic acid (10 c.c.) containing concentrated sulphuric acid (0·05 c.c.) after 72 hr. yielded 1 : 3 : 5-*trimethoxy*-2-(1 : 2 : 3 : 4-*tetrahydro*-1-*naphthyl*)*benzene* as irregular rhombs (0·69 g.; from light petroleum), m. p. 82—83° (Found : C, 76·3; H, 7·3. $C_{19}H_{22}O_3$ requires C, 76·5; H, 7·7%).

Reaction of 2-*Phenylbutan*-2-*ol and its Hydrogen Phthalate, with Sodium Toluene*-p-*sulphinate.*—After 72 hr., a solution of 2-phenylbutan-2-ol (0·5 g.) and sodium toluene-*p*-sulphinate (0·80 g.) in 90% formic acid (20 c.c.) was poured over crushed ice, yielding 1-*ethyl*-1-*phenylpropyl* p-*tolyl sulphone* (0·78 g.) as tablets (from aqueous methanol), m. p. 63—64° (Found : C, 71·1; H, 7·1; S, 11·1. $C_{17}H_{20}O_2S$ requires C, 70·8; H, 6·9; S, 11·1%).

Similarly, the hydrogen phthalate (0·50 g.) in acetone (3·0 c.c.) and sodium toluene-*p*-sulphinate (0·50 g.) in 90% formic acid (15 c.c.) after 72 hr. had deposited crystals of phthalic acid (0·17 g.). The supernatant solution was poured over ice, yielding the sulphone (0·25 g.; from aqueous methanol), m. p. and mixed m. p. 63—64°.

Reaction between Organic Peroxides and 1 : 3 : 5-*Trimethoxybenzene and* 1 : 3 : 5-*Triethoxybenzene.*—(i) *Xanthhydryl hydroperoxide.* Xanthhydryl hydroperoxide (0·5 g.) in chloroform (5·0 c.c.) was added to 1 : 3 : 5-trimethoxybenzene (0·40 g.) in glacial acetic acid (10 c.c.). Next day the mixture was poured over ice, yielding 1 : 3 : 5-trimethoxy-2-xanthhydrylbenzene (0·57 g.; from butanol), m. p. and mixed m. p. 159—160°. Similarly, 1 : 3 : 5-triethoxybenzene yielded 1 : 3 : 5-triethoxy-2-xanthhydrylbenzene (from butanol), m. p. and mixed m. p. 157·5—158·5°.

(ii) *Xanthhydryl peroxide.* A mixture of xanthhydryl peroxide (0·52 g.) in chloroform (5 c.c.) and 1 : 3 : 5-trimethoxybenzene (0·43 g.) in acetic acid (10 c.c.), after 72 hr. yielded 1 : 3 : 5-trimethoxy-2-xanthhydrylbenzene (from butanol; 0·79 g.), m. p. and mixed m. p. 159—160°.

(iii) *Bis*(*di*-p-*methoxyphenylmethyl*) *peroxide.* A mixture of the peroxide (0·38 g.) in chloroform (5·0 c.c.) and 1 : 3 : 5-triethoxybenzene (0·36 g.) in acetic acid (5·0 c.c.) was poured, after 14 days, over ice, and the precipitate crystallised from propanol, yielding 2 : 4 : 6-triethoxy-4′ : 4″-dimethoxytriphenylmethane (0·21 g.), m. p. and mixed m. p. 108—109°. Some red oil was also formed which was probably a decomposition product of the peroxide caused by oxygen–oxygen heterolysis.

(iv) 1 : 2 : 3 : 4-*Tetrahydro*-1-*naphthyl hydroperoxide.* The hydroperoxide (0·25 g.) in chloroform (5·0 c.c.) was added to a solution of 1 : 3 : 5-trimethoxybenzene (0·30 g.) in acetic acid (5·0 c.c.) containing concentrated sulphuric acid (0·05 c.c.). After 96 hr. the mixture was poured over ice and the oil which separated was extracted successively with light petroleum and with ether. From the light petroleum extract, 1 : 3 : 5-trimethoxy-2-(1 : 2 : 3 : 4-tetrahydro-1-naphthyl)benzene (0·05 g.) was recovered, having m. p. and mixed m. p. 81·5—82·5°. The ethereal extract yielded a dark red oil, from which an acid, probably γ-*o*-hydroxyphenylbutyric acid, was isolated, with an unsharp m. p. of 57—61°.

Reaction between Organic Peroxides and Sodium Toluene-p-*sulphinate.*—(i) *Xanthhydryl peroxide.* From a solution of xanthhydryl peroxide (0·2 g.) and sodium toluene-*p*-sulphinate (0·22 g.) in acetic acid (15 c.c.), colourless crystals began to separate after 2 hr. Recrystallisation from ethanol gave *p*-tolyl xanthhydryl sulphone (0·26 g.), m. p. and mixed m. p. 214—215° to a red liquid.

(ii) 1 : 2 : 3 : 4-*Tetrahydro*-1-*naphthyl xanthhydryl peroxide.* A suspension of the peroxide (0·42 g.) in a solution of sodium toluene-*p*-sulphinate (0·28 g.) in acetic acid (7 c.c.) was stirred for 2 hr. and then diluted with water, yielding *p*-tolyl xanthhydryl sulphone (0·48 g.) which was recrystallised from ethanol when it showed m. p. and mixed m. p. 214°.

(iii) tert.-*Butyl xanthhydryl peroxide.* A solution of *tert*.-butyl xanthhydryl peroxide (1·0 g.) and sodium toluene-*p*-sulphinate (0·80 g.) in acetic acid (10 c.c.) at 50° immediately began to deposit crystals of *p*-tolyl xanthhydryl sulphone. After 1 hr., water (15 c.c.) was added yielding more sulphone (from ethanol; in all, 1·06 g., 86%), m. p. and mixed m. p. 214—215°. The filtrate, after being neutralised with sodium hydrogen carbonate, was extracted with light petroleum, yielding *tert*.-butyl hydroperoxide, which was identified as 1-*tert*.-butyl hydrogen 1-monoperphthalate (from ether–light petroleum; 50 mg.), m. p. and mixed m. p. 102—103°.

(iv) tert.-*Butyl triphenylmethyl peroxide.* On the addition of one drop of concentrated sulphuric acid to a solution of *tert*.-butyl triphenylmethyl peroxide (50 mg.) and sodium toluene-*p*-sulphinate (50 mg.) in acetic acid (5 c.c.), a yellow colour developed. After 1·5 hr. crystals began to separate. Next day these were filtered off (50 mg.) and recrystallised from benzene–light petroleum, yielding *p*-tolyl triphenylmethyl sulphone, m. p. and mixed m. p. 173—174°.

(v) *Bis*(*di*-p-*methoxyphenylmethyl*) *peroxide.* A red solution of the peroxide (0·20 g.) in glacial acetic acid (3 c.c.) containing one drop of concentrated sulphuric acid, was added to sodium toluene-*p*-sulphinate (0·20 g.) in acetic acid (2 c.c.); the colour slowly faded. After 45 min. the solution was poured over crushed ice, yielding di-*p*-methoxyphenylmethyl *p*-tolyl sulphone (from ethanol, 0·18 g.), m. p. and mixed m. p. 102—104°. In the absence of sulphuric acid, the peroxide was recovered from a similar reaction mixture after 1 hr.

(vi) tert.-*Butyl* 1-*methyl*-1-*phenylpropyl peroxide.* The peroxide (2·22 g., 1 mol.) which is insoluble in acetic and formic acids, was stirred with a solution of sodium toluene-*p*-sulphinate (1·78 g., 1 mol.) in 90% formic acid (50 c.c.) for 8 hr., the solution becoming homogeneous. After a further 48 hr. the mixture was poured over ice, yielding an oil which solidified. Recrystallisation from aqueous methanol yielded 1-methyl-1-phenylpropyl *p*-tolyl sulphone (0·98 g.), m. p. and mixed m. p. 65°.

(vii) 1 : 2 : 3 : 4-*Tetrahydro*-1-*naphthyl hydroperoxide.* After 16 hr. a solution of the hydroperoxide (0·5 g.) and sodium toluene-*p*-sulphinate (0·7 g.) in 98% formic acid (10 c.c.) had deposited a buff-coloured precipitate which did not melt below 300° and was insoluble in the common organic solvents but dissolved in water; from its aqueous solution the parent acid could be obtained by acidification; it was thus probably the acid decomposition product of the peroxide, γ-*o*-hydroxyphenylbutyric acid. The filtrate, on treatment with water, yielded toluene-*p*-sulphonic acid (0·10 g.), m. p. 104—105°. The hydroperoxide had thus apparently been reduced by the sulphinate. From a neutral solution the reduction product was isolated : a suspension of the hydroperoxide (2·0 g.) in a solution of sodium toluene-*p*-sulphinate (4·2 g.) in water (30 c.c.) was shaken for 5 hr. From the mixture, an oil was isolated with b. p. 92—94°/0·3 mm. (0·25 g.), which was identified as 1 : 2 : 3 : 4-tetrahydro-1-naphthol by the preparation of its hydrogen phthalate, m. p. and mixed m. p. 112°. No sulphone was isolated, but an undistillable viscous residue was obtained, which was probably polymerised 1 : 2-dihydronaphthalene.

(viii) 1-*Methyl*-1-*phenylpropyl hydroperoxide.* A solution of 1-methyl-1-phenylpropyl hydroperoxide (0·30 g.) and sodium toluene-*p*-sulphinate (0·42 g., 1 mol.) in 98% formic acid (13 c.c.), after 20 hr. was poured over ice, and the resulting emulsion neutralised with dilute sodium hydroxide. An ethereal extract yielded a colourless oil (0·14 g.), b. p. 102°/14 mm., identified as 1-methyl-1-phenylpropanol as follows. The oil (0·14 g.) was heated with 1-naphthyl *iso*cyanate (0·14 g.) in ligroin (5 c.c.) for 1 hr., and the whole filtered hot. On cooling, crystals separated, which were recrystallised from light petroleum (b. p. 60—80°), yielding 1-methyl-1-phenylpropyl 1-naphthylurethane, m. p. and mixed m. p. 128—129°. Hawkins (*J.*, 1949, 2076) reports m. p. 129—130·5°. We are indebted to Dr. E. G. E. Hawkins for the details of this reaction.

Reaction between Xanthhydryl Peroxide and Urea.—A suspension of the peroxide (0·181 g.) in a solution of urea (0·20 g., excess) in glacial acetic acid (30 c.c.) became homogeneous after 2 min. at 70°. After 3 days at room temperature, water (150 c.c.) was added and the precipitated material filtered off through a weighed sintered-glass filter and washed with water (100 c.c.), giving *s*-dixanthhydrylurea (0·182 g., 94%), m. p. and mixed m. p. 270—272°. Titration of the combined filtrate and washings with standard potassium permanganate solution showed it to contain 96% of the theoretical amount of hydrogen peroxide.

Reaction between Xanthhydryl Peroxide and Ethyl Acetoacetate.—After 45 min. a solution of xanthhydryl peroxide (0·20 g.) and ethyl acetoacetate (0·26 g.) in acetic acid (5 c.c.) containing concentrated sulphuric acid (0·05 c.c.) was poured on ice, yielding ethyl xanthhydrylacetoacetate (from light petroleum; 0·34 g.), m. p. and mixed m. p. 88—89°.

Reaction between Xanthhydryl Peroxides and Acetone.—(i) tert.-*Butyl xanthhydryl peroxide.* A solution of *tert.*-butyl xanthhydryl peroxide (0·7 g.) in acetone (4 c.c.) containing concentrated sulphuric acid (0·1 c.c.), rapidly became deep red. After 60 hr. the mixture was poured over ice, yielding xanthhydrylacetone (from aqueous ethanol; 0·68 g.), m. p. 101—102° (Found: C, 80·8; H, 6·1. Calc. for $C_{16}H_{14}O_2$: C, 80·6; H, 5·9%). Fosse and Robyn (*Bull. Soc. chim.*, 1906, **35**, 1013) report m. p. 101—102° for this compound prepared by the hydrolysis of ethyl xanthhydrylacetoacetate.

(ii) tert.-*Amyl xanthhydryl peroxide.* Similarly, after 40 hr., a solution of *tert.*-amyl xanthhydryl peroxide (1·0 g.) in acetone (3 c.c.) containing concentrated sulphuric acid (0·05 c.c.) yielded xanthhydrylacetone (1·05 g.) which, recrystallised from aqueous ethanol, had m. p. and mixed m. p. 101—102° (Found: C, 80·8; H, 5·7%).

Disproportionation of Xanthhydryl Hydroperoxide.—Xanthhydryl hydroperoxide (0·98 g.) was warmed at 50° in glacial acetic acid (10 c.c.), and the mixture diluted with water, yielding xanthhydryl peroxide (from ethanol; 0·72 g.) as white needles, m. p. 152—153° (Found: C, 78·8; H, 4·8. Calc. for $C_{26}H_{18}O_4$: C, 79·2; H, 4·6%).

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