133. *Organic Peroxides. Part VI.* A Stereochemical Investigation of the Preparation and Reactions of 1-Phenylethyl Hydroperoxide.*

By Alwyn G. Davies and R. Feld.

The acid-catalysed oxidation of optically active 1-phenylethanol (I) to 1-phenylethyl hydroperoxide (II) with 90% hydrogen peroxide gives a value of α_{II}/α_I (α = optical rotation) varying between $-0{\cdot}069$ and $-0{\cdot}146$ in different preparations. In the reduction of the hydroperoxide back to the alcohol (III) directly or through its triphenylmethyl derivative, with a wide variety of reagents, α_{III}/α_{II} is constant ($+0{\cdot}28$ to $+0{\cdot}33$) within the experimental error, but α_{III}/α_I varies between $-0{\cdot}019$ and $-0{\cdot}036$, because of variation in α_{II}/α_I. It is concluded that the reductions all involve 100% retention of configuration and therefore the oxidation of 1-phenylethanol proceeds with inversion accompanied by a high degree of racemisation. This supports our conclusion that the alcohol is oxidised principally by an S_N1-like mechanism.

We have previously presented evidence (summarised in Part V [1]) that the acid-catalysed oxidation of alcohols with hydrogen peroxide or alkyl hydroperoxides proceeds by alkyl–oxygen heterolysis of the alcohol, usually by an S_N1 mechanism. With optically active alcohols, which do not carry groups which assist retention of configuration, this mechanism usually involves racemisation accompanied by varying amounts of stereochemical inversion,[2] and we have shown that active 1 : 2 : 3 : 4-tetrahydro-1-naphthol yields the inactive hydroperoxide. As the reactivity of alcohols by this mechanism, and the degree of racemisation in the intermediate carbonium ion, are both dependent on the stability of the ion, it follows that the less reactive alcohols might retain some optical asymmetry. We have accordingly investigated the stereochemical course of the reaction of a number of optically active alcohols (and their esters and ethers) with hydrogen peroxide; the results for active 1-phenylethanol are now reported.

The problem of relating the configuration of reactant and product would be simple if the hydroperoxide could be reduced back to the alcohol by a reaction which was known unambiguously to involve simple O–O fission and therefore retention of configuration of the alkyl group. No compelling evidence, however, is available of the mechanism of any of the possible reductions. Williams and Mosher [3] assumed that catalytic hydrogenation

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* Part V, *J.*, 1955, 2471. A preliminary note of the present work has appeared in *Chem. and Ind.*, 1954, 1322.

[1] Bassey, Bunton, Davies, Lewis, and Llewellyn, *J.*, 1955, 2471.

[2] Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 386.

[3] Williams and Mosher, *J. Amer. Chem. Soc.*, 1954, **76**, 3495.

over palladium and the reaction with lithium aluminium hydride[4] followed this simple course, although both reactions in principle might involve some racemisation.[5] Kornblum and de la Mare[6] showed that the pyrolysis of *tert.*-butyl 1-phenylethyl peroxide in the presence of thiophenol as a hydrogen donor gave, *via* the alkoxy-radical, the alcohol with little or no racemisation in the 1-phenylethyl group; similarly, if the hydrogen sulphite reduction of a hydroperoxide proceeds through the alkoxy-radical as Kharasch and his co-workers suggest,[7] the alkyl group might be expected to retain its asymmetry, although this result might be dependent upon pH.[8] In the present work, the problem has been overcome by correlating the optical results of reduction, a large variety of reagents being used.

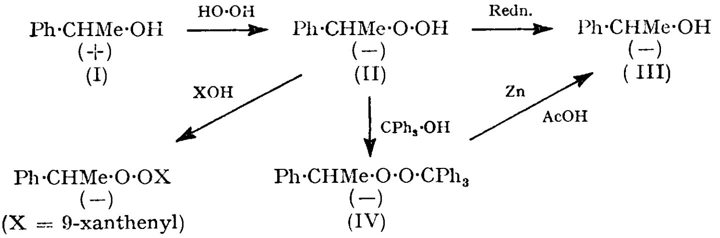
Optically active (+)1-phenylethanol (I) reacted with 90% hydrogen peroxide in the presence of sulphuric acid to yield active (—)1-phenylethyl hydroperoxide (II) with a value of α_{II}/α_{I} varying between —0·069 and —0·146 (see Table 2), the negative sign indicating inversion of sign of rotation; the product was shown to racemise only slowly under the reaction conditions. The active hydroperoxide was then reduced to the (—) alcohol (III) with a wide variety of reagents, giving a positive value of α_{III}/α_{II} which was constant within the experimental error (Table 1), but with values of α_{III}/α_{I} varying between —0·019 and —0·036, because of variation in α_{II}/α_{I}.

TABLE 1. *Reduction of active* 1-*phenylethyl hydroperoxide* (II) *and* 1-*phenylethyl triphenylmethyl peroxide* (IV).

Peroxide ...	(II)						(IV)
Reagent ...	Na_2SO_3	$LiAlH_4$	Zn–HOAc	$SnCl_2$	$C_7H_7{\cdot}SO_2Na$	H_2–Pt	Zn–HOAc
α_{III}/α_{II}	+0·29, +0·31	+0·25[a]	+0·28	+0·32	+0·33	+0·28	+0·28

[a] This low value is probably caused by a fraction of the reduction proceeding *via* acetophenone—see later.

When the hydroperoxide (II) obtained from the optically pure alcohol (I) was alkylated with triphenylmethanol or xanthhydrol, it gave the corresponding partially racemised derivatives whose optical purity could be increased by fractional crystallisation. Active 1-phenylethyl triphenylmethyl peroxide (IV), which had not been fractionated, was reduced to 1-phenylethanol (III) with zinc and acetic acid; α_{III}/α_{II} is recorded in Table 1.



The Reduction of the Peroxides.—It would be most surprising if the wide variety of reagents used in the eight methods of reduction all gave the same degree of racemisation during reaction. Similarly, it is difficult to envisage all these reductions proceeding with 100% inversion of configuration. The value of α_{III}/α_{II}, which is constant within the experimental error, must therefore imply that all these reactions proceed with essentially 100% retention of configuration in the 1-phenylethyl group. Powerful support for this is afforded by the demonstration[9] that the reduction of 1-phenylethyl hydroperoxide with sodium [^{18}O]sulphite in [^{18}O]water yields the isotopically normal alcohol; it thus appears that the alkyl–oxygen bond remains intact during the reduction. Similarly the fact that

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[4] Cf. Russell, *J. Amer. Chem. Soc.*, 1953, **75**, 5011.

[5] (*a*) Davies and Elton, *J.*, 1952, 3298; (*b*) Kornblum and de la Mare, *J. Amer. Chem. Soc.*, 1951, **73**, 851.

[6] *Idem, ibid.*, 1952, **74**, 3079.

[7] Kharasch and co-workers, *J. Org. Chem.*, 1951, **16**, 113; *J. Amer. Chem. Soc.*, 1939, **61**, 3092.

[8] Halperin and Taube, *ibid.*, 1952, **74**, 380.

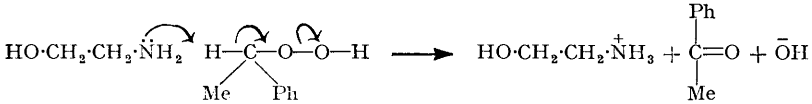
[9] M. Bassey, unpublished work.

no trace of 1-phenylethyl *p*-tolyl sulphone could be isolated from the reduction of the hydroperoxide with sodium toluene-*p*-sulphinate implies that the reaction does not proceed by unimolecular alkyl–oxygen heterolysis.

We assume therefore that all these reductions proceed with 100% retention of configuration. It follows that 1-phenylethanol and 1-phenylethyl hydroperoxide of the same sign of rotation have corresponding configurations (cf. heptan-2-ol and 1-methylhexyl hydroperoxide [3]), and the maximum rotation of 1-phenylethanol being assumed to be $\alpha_D = 44{\cdot}2°$ (*l*, 1·0),[10] 1-phenylethyl hydroperoxide has a maximum rotation of α_D = about 140° (*l*, 1·0).

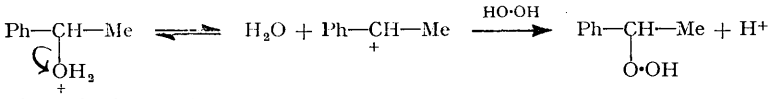
Kharasch and his co-workers' suggestion [7] that the reduction of 1-methyl-1-phenylethyl hydroperoxide with sodium hydrogen sulphite proceeds by a mechanism involving the $PhMe_2CO{\cdot}$ radical, was based on the observation that the addition of styrene to the reaction mixture permits isolation of 2-phenylethanesulphonic acid and 2-hydroxy-2-phenylethanesulphonic acid. Halperin and Taube,[8] however, have shown that in the acid reduction of $[^{18}O_2]$hydrogen peroxide with sulphite, *both* labelled oxygen atoms are located in the sulphate which is formed. They suggest that this reaction is heterolytic and proceeds by the formation and subsequent intramolecular rearrangement of peroxysulphurous acid, $H^{18}O{\cdot}^{18}O{\cdot}SO{\cdot}OH$. If a similar mechanism applied to the sulphite reduction of 1-phenylethyl hydroperoxide it would involve alkyl–oxygen fission in the peroxy-ester, $CHMePh{\cdot}^{18}O{\cdot}^{18}O{\cdot}SO{\cdot}OH$, with a stereochemical result probably differing from 100% retention. We attempted to reduce the hydroperoxide under acid conditions, but at pH 0 and 1 obtained only acetophenone; at pH 5 a mixture of acetophenone and 1-phenylethanol was obtained.

Acetophenone was also isolated from the attempted reduction of 1-phenylethyl hydroperoxide with 2-aminoethanol [11] and of 1-phenylethyl triphenylmethyl peroxide with sodium and ethanol or methanol. This presumably arises by base-catalysed O–O heterolysis of the type described by Kornblum and de la Mare,[5b] *e.g.*:



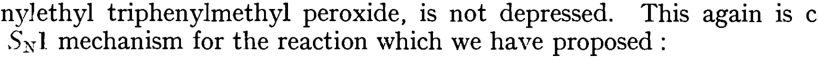
$$\mathrm{HO{\cdot}CH_2{\cdot}CH_2{\cdot}\ddot{N}H_2\ \ H{-}\underset{Me\quad Ph}{C}{-}O{-}O{-}H \longrightarrow HO{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{+}{N}H_3 + \overset{Ph}{\underset{Me}{C}}{=}O + \bar{O}H}$$

The Oxidation of the Alcohol.—If it is accepted then that the hydroperoxide is reduced with 100% retention of configuration, the low, negative, and variable values of α_{III}/α_I, which appear in the final column of Table 2, express the percentage of retention of configurational purity occurring during the oxidation of 1-phenylethanol which proceeds with inversion accompanied by a high degree of racemisation.* This is compatible with our suggestion that the reaction proceeds through the intermediate formation of the 1-phenylethylium ion:



$$\mathrm{Ph{-}\underset{\overset{+}{O}H_2}{C}H{-}Me \rightleftharpoons H_2O + Ph{-}\underset{+}{C}H{-}Me \xrightarrow{HO{\cdot}OH} Ph{-}\underset{O{\cdot}OH}{C}H{-}Me + H^+}$$

The oxidation of triphenylmethanol with 1-phenylethyl hydroperoxide involves no loss of asymmetry in the 1-phenylethyl group, as the value of α_{III}/α_{II}, obtained in reductions of 1-phenylethyl triphenylmethyl peroxide, is not depressed. This again is compatible with the S_N1 mechanism for the reaction which we have proposed:



$$\mathrm{Ph_3C{-}\overset{+}{O}H_2 \rightleftharpoons H_2O + Ph_3\overset{+}{C} \xrightarrow{PhCHMe{\cdot}O{\cdot}OH} Ph_3CO{\cdot}O{\cdot}CHPhMe + H^+}$$

The fact that the hydroperoxide obtained from the fully active alcohol gives optically impure triphenylmethyl and 9-xanthenyl derivatives, also therefore establishes that the initial oxidation of 1-phenylethanol involves some racemisation.

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* The active hydroperoxide can be converted into its sodium salt and recovered without loss of optical purity; we therefore do not consider that any optical asymmetry arises because of restriction of rotation about the O–O bond in the skew structure of the peroxide.[12]

[10] Downer and Kenyon, *J.*, 1939, 1156.

[11] Cf. Capp and Hawkins, *J.*, 1953, 4106.

[12] Davies, *Discuss. Faraday Soc.*, 1953, **14**, 140.

Two other reports of work on the stereochemistry of the preparation of peroxides have appeared. Kornblum and de la Mare [6] obtained optically active *tert.*-butyl 1-phenylethyl peroxide by the interaction of potassium *tert.*-butyl peroxide and active 1-phenylethyl bromide, and Williams and Mosher [3] prepared active 1-methylhexyl hydroperoxide by the alkaline perhydrolysis of active 1-methylhexyl methanesulphonate. By the reduction of these peroxides to the corresponding active alcohols by methods (see above) which were assumed not to affect the asymmetric centre of the molecule, it was shown in both cases that the oxidation reactions involved a high degree of stereochemical inversion, and therefore followed an S_N2 mechanism.

Further studies on the stereochemical course of the preparation and reactions of organic peroxides are in progress. We have obtained evidence that the S_Ni mechanism may be of importance in the oxidation of some alcohols and carboxylic esters.

EXPERIMENTAL

Unless otherwise stated, all values of α_D of liquids were recorded on the undiluted specimens in 1-dm. tubes at temperatures between 18° and 22°.

1-Phenylethanol (I) was resolved by Downer and Kenyon's method.[10]

Active 1-*Phenylethyl Hydroperoxide* (II).—In a typical experiment, a mixture of optically active 1-phenylethanol (3·0 g.) and 90% hydrogen peroxide (12 c.c.) containing concentrated sulphuric acid (0·1 g.) was stirred for 1 hr. at 0° and then for 5 hr. at room temperature; precautions were taken against explosion. Water (50 c.c.) was added, the product extracted three times with ether (5 c.c.), and the extract washed with saturated aqueous sodium hydrogen carbonate and with water, and dried (Na_2SO_4). The ether was removed at the pump and the residue distilled, yielding optically active 1-*phenylethyl hydroperoxide* (2·76 g.), b. p. 66°/0·5 mm. (Found: C, 70·2; H, 6·9. $C_8H_{10}O_2$ requires C, 69·8; H, 7·3%).

This preparation was repeated a number of times on this scale partly because the hydroperoxide slowly decomposed, but more particularly to minimise the explosion hazard. The results are recorded in Table 2.

TABLE 2.

1-Phenylethanol (I)		1-Phenylethyl hydroperoxide (II)			Retention of configurational
Weight (g.)	α_D	Weight (g.)	α_D	α_{II}/α_I	purity, %
2·00	+43·30°	1·4	−4·80°	−0·111	−3·5
2·00	−43·30	1·40	+5·20	−0·120	−3·8
3·50	−41·80	3·20	+4·41	−0·105	−3·3
2·00	"	1·69	+4·16	−0·101	−3·1
1·00	"	0·79	+4·14	−0·099	−3·1
5·00	+14·20	4·10	−1·53 (*a*)	−0·108	−3·4
4·00	"	3·64	−1·87	−0·132	−4·2
2·50	"	2·10	−2·05	−0·144	−4·6
2·50	"	2·10	−1·58	−0·111	−3·5
8·00	"	6·40	−1·39 (*b*)	−0·098	−3·1
2·00	"	1·40	−0·98	−0·069	−2·2

Specimens *a* and *b* were combined, giving the hydroperoxide, α_D^{18} −1·45°, which was used in some of the following experiments.

Active 1-*Phenylethyl Triphenylmethyl Peroxide* (IV).—(i) Triphenylmethanol (1·90 g.) in acetic acid (10 c.c.) containing concentrated sulphuric acid (0·1 g.) was added to 1-phenylethyl hydroperoxide (0·83 g.; α_D^{18} − 1·45°) in acetic acid (10 c.c.). After 2 hr., iced water was added, and active 1-*phenylethyl triphenylmethyl peroxide* (IV) (2·35 g.) was obtained, m. p. 73—77°, $[\alpha]_D^{21}$ −0·94° (*l*, 2; *c*, 5·8 in $CHCl_3$). Recrystallisation from ethanol effected partial separation of the less soluble, higher melting, peroxide, m. p. 76—78°, $[\alpha]_D^{22}$ −0·64° (*l*, 1; *c*, 6·5 in $CHCl_3$), from the more active compound, m. p. 60—63°, $[\alpha]_D^{22}$ −2·63° (*l*, 0·5; *c*, 4·6 in $CHCl_3$). From a second recrystallisation of the fraction, m. p. 76—78°, the racemic peroxide was obtained, m. p. 85° (Found: C, 85·2; H, 6·2. Calc. for $C_{27}H_{24}O_2$: C, 85·2; H, 6·35%).[13]

The preparation was repeated with the following results:

(ii) The hydroperoxide, α_D^{18} −1·87° (3·64 g.), gave the peroxide (9·93 g.), m. p. 79—81°, $[\alpha]_D^{14}$ −1·21° (*l*, 2; *c*, 4·95 in $CHCl_3$).

(iii) The hydroperoxide, α_D^{21} +5·20°, gave the peroxide, m. p. 78—83°, $[\alpha]_D^{18}$ +4·3° (*l*, 0·5; *c*, 5·3 in $CHCl_3$), which on recrystallisation from ethanol gave a more soluble fraction, $[\alpha]_D^{17}$

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[13] Cf. Davies, Foster, and White, *J.*, 1954, 2200.

+21·1°, m. p. 78—83°, and a less soluble fraction, m. p. 85—86°, $[\alpha]_D^{15}$ +2·6° (*l*, 0·5; *c*, 0·3 in $CHCl_3$).

(iv) The hydroperoxide, α_D^{21} −2·05° (1·25 g.), gave the peroxide (3·05 g.), $[\alpha]_D^{18}$ −1·35° (*l*, 2; *c*, 4·82 in $CHCl_3$).

Active 1-*Phenylethyl* 9-*Xanthenyl Peroxide*.—(i) The hydroperoxide (1·61 g.), α_D^{18} −1·45°, in acetic acid (5 c.c.) was added to xanthhydrol (2·3 g.) in acetic acid (10 c.c.). After 1·5 hr. the mixture was poured on ice–water (50 c.c.) yielding *active* 1-*phenylethyl* 9-*xanthenyl peroxide* (3·3 g.), m. p. 81—84°, $[\alpha]_D^{16}$ −0·72° (*l*, 2; *c*, 5·50 in $CHCl_3$). Recrystallisation from light petroleum gave the pure (±)-peroxide, m. p. and mixed m. p. 84—86°, and a more soluble fraction of the (−)-peroxide, m. p. 82—84°, $[\alpha]_D^{21}$ −1·03° (*l*, 0·5; *c*, 5·8 in $CHCl_3$).

(ii) In a second experiment the hydroperoxide, α_D^{21} +5·20°, gave the peroxide, m. p. 79—82°, $[\alpha]_D^{17}$ +4·2° (*l*, 0·5; *c*, 4·6 in $CHCl_3$), which by recrystallisation was separated into two fractions: (*a*) m. p. 84—86°, $[\alpha]_D^{15}$ +2·5° (*l*, 0·5; *c*, 2·9 in $CHCl_3$), and (*b*) m. p. 81—84°, $[\alpha]_D^{15}$ +6·7° (*l*, 0·5; *c*, 0·3 in $CHCl_3$).

Optical Stability of 1-*Phenylethyl Hydroperoxide under Preparative Conditions*.—The active hydroperoxide (0·79 g.), α_D^{20} +4·14°, n_D^{20} 1·5251, was stirred for 30 min. with 90% hydrogen peroxide (5 c.c.) containing concentrated sulphuric acid (0·1 g.). The hydroperoxide (0·68 g.) was recovered in the usual way, and had b. p. 50°/0·001 mm., α_D^{16} +3·94°, n_D^{20} 1·5246.

Reductions of Active 1-*Phenylethyl Hydroperoxide*.—(i) *With sodium sulphite.* The hydroperoxide (II; 2·0 g.), α_D^{18} −1·45°, was shaken for 6 hr. with a solution of sodium sulphite heptahydrate (9·0 g., 2·5 mols.; in 70 c.c. of water). The alcohol was extracted with ether, and the extract washed and dried, yielding 1-phenylethanol (III; 1·3 g.), b. p. 134—137°/120 mm., α_D^{17} −0·42°, characterised as its hydrogen phthalate, m. p. 106—108°. In a second experiment the hydroperoxide (1·49 g.), α_D^{21} +5·20°, gave the alcohol (0·7 g.), α_D^{21} +1·60°, b. p. 95—98°/20 mm. n_D^{20} 1·5265.

(ii) *With lithium aluminium hydride.* The hydroperoxide (1·0 g.), α_D −1·58°, in ether (5 c.c.) was added dropwise to a stirred suspension of lithium aluminium hydride (0·31 g., 1·1 mol.) in ether (10 c.c.) and a vigorous reaction took place. The mixture was then heated under reflux for 30 min., and the metal salts decomposed by the addition of water and then dilute sulphuric acid. From the ethereal layer, 1-phenylethanol was recovered (0·78 g., 88%). b. p. 112°/15 mm., α_D^{18} −0·40°, and characterised as its hydrogen phthalate, m. p. 108°.

(iii) *With zinc and acetic acid.* Zinc dust (2·0 g.) was added to a solution of the hydroperoxide (1·4 g.), α_D^{22} −0·98°, in glacial acetic acid (5 c.c.). No reaction had occurred after 30 min., and the solution still gave a positive test for peroxide (potassium iodide–starch). On addition of water (1 c.c.; dropwise) to the cooled mixture a vigorous reaction took place, and the solution no longer contained peroxide. The mixture was poured into water (50 c.c.), neutralised with sodium hydrogen carbonate, and filtered from excess of zinc, and the filtrate extracted with ether. The washed, dried extract yielded 1-phenylethanol (1·05 g.), b. p. 89—90°/1 mm., α_D^{16} −0·27°.

(iv) *With stannous chloride.*[14] The hydroperoxide (1·0 g.), α_D^{20} +4·41°, in acetic acid (5 c.c.) was added to approximately 0·5N-stannous chloride solution (5·65 g. of $SnCl_2,2H_2O$; 7·5 c.c. of concentrated hydrochloric acid; 92·5 c.c. of water). After 6 hr. at room temperature the solution was extracted with ether (3 × 5 c.c.). The combined extracts were washed with saturated aqueous sodium hydrogen carbonate and with water, and dried; distillation gave 1-phenylethanol (0·62 g.), α_D^{20} +1·41°, n_D^{25} 1·5249.

(v) *With sodium toluene*-p-*sulphinate.* The hydroperoxide (0·8 g.), α_D^{20} +4·41°, in ether (5 c.c.) was shaken with a solution of sodium toluene-*p*-sulphinate (2·58 g., 2 mols.) in water (30 c.c.). The organic layer still gave a strong peroxide test; pyridine (2 c.c.) was added and the shaking continued for a further 2 hr.; no peroxide then remained. The mixture was neutralised with dilute sulphuric acid and extracted with ether. Distillation gave 1-phenylethanol (0·43 g.), α_D^{19} +1·44°, n_D^{25} 1·5253.

(vi) *With hydrogen over platinum.* The hydroperoxide (0·79 g.), α_D^{21} −2·05°, in ether (15 c.c.) was shaken in an atmosphere of hydrogen in the presence of reduced platinum oxide (0·06 g.). After a rapid initial reaction the theoretical volume of hydrogen (128 c.c. at S.T.P.) was absorbed during 4 hr. 1-Phenylethanol was recovered in quantitative yield, b. p. 102—104°/14 mm., α_D^{18} −0·58°, n_D^{20} 1·5250.

The hydroperoxide was recovered in 45% yield after being shaken for 6 hr. with an excess of a 25% aqueous solution of sodium nitrite in the presence of a little ether to increase the mutual solubility of the phases.

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[14] Cf. Barnard and Hargreaves, *Analyt. Chim. Acta*, 1951, **5**, 476.

Other Reactions of 1-*Phenylethyl Hydroperoxide*.—(i) *With* 2-*aminoethanol*. A mixture of aminoethanol (8 g., 6 mols.) and 1-phenylethyl hydroperoxide (2·0 g., 1 mol.) was warmed to 70°; a vigorous reaction occurred, the internal temperature rising to 120°. After a further 15 min. at 70° the reaction mixture, which then gave no test for peroxide, was poured on an excess of ice–dilute sulphuric acid. An ethereal extract yielded acetophenone (1·3 g.), b. p. 102°/14 mm. (semicarbazone, m. p. and mixed m. p. 201—203°).

(ii) *With sulphur dioxide at* pH 0 *and* 1. A violent reaction occurred when the hydroperoxide (1·5 g.) in ether (3 c.c.) was added dropwise to 1N-hydrochloric acid (50 c.c.) saturated with sulphur dioxide at 0°. After 2 hours' stirring, the mixture was extracted with ether, yielding an oil, b. p. 92°/12 mm. (0·6 g.), which gave a semicarbazone, m. p. 201—203°, undepressed on admixture with acetophenone semicarbazone. A similar result was obtained at pH 1.

(iii) *With sulphur dioxide at* pH 4·8. Acetic acid (*ca.* 12 c.c.) was added to a solution of sodium sulphite heptahydrate (7·5 g.) and sodium acetate trihydrate (1·5 g.) in water (100 c.c.), giving a mixture of pH 4·8. 1-Phenylethyl hydroperoxide (1·5 g.) in ether (5 c.c.) was added, and the mixture stirred for 3 hr. An ethereal extract yielded a mixture (0·95 g.) of acetophenone and 1-phenylethanol, which gave 1-phenylethyl *N*-phenylcarbamate, m. p. 93—94°, in 42% yield and acetophenone semicarbazone, m. p. and mixed m. p. 200—201°, in 40% yield.

Reductions of 1-*Phenylethyl Triphenylmethyl Peroxide*.—(i) *With zinc and acetic acid*. Zinc dust (5 g.) was added to a solution of 1-phenylethyl triphenylmethyl peroxide (4·93 g.), $[\alpha]_D^{14}$ $-1·21°$ (*l*, 1; *c*, 4·9 in $CHCl_3$), in warm acetic acid (40 c.c.) and water (5 c.c.). After 30 min. at 80°, water was added and the solution made just acidic by successive additions of sodium hydroxide and a little hydrochloric acid. An ethereal extract yielded 1-phenylethanol (0·92 g.), b. p. 90—92°/15 mm., α_D^{18} $-0·52°$.

(ii) *With zinc and hydrochloric acid*. The peroxide (4·0 g.) in ethanol (96%; 20 c.c.) was reduced with zinc dust (4·0 g.) and concentrated hydrochloric acid (10 c.c.), at 50° to keep the peroxide in solution. When the metal was completely dissolved the mixture was steam-distilled, yielding 1-phenylethanol (0·6 g.), b. p. 70°/1·5 mm. (hydrogen phthalate, m. p. 103—105°, mixed m. p. 105—106°).

From an attempt to reduce 1-phenylethyl 9-xanthenyl peroxide with lithium aluminium hydride by a method similar to that described for 1-phenylethyl hydroperoxide, the peroxide (1·92 g. from 2·20 g.) was recovered, even when the period of heating of the reaction mixture was extended to 3 hr.[4] No reaction occurred with 1-phenylethyl triphenylmethyl peroxide under the same conditions.

Other Reactions of 1-*Phenylethyl Triphenylmethyl Peroxide*.—(i) *With sodium and ethanol*. The peroxide (2·8 g.) in dry ether (25 c.c.) was added to sodium powder (1·65 g.) under dry ether (25 c.c.). After 5 hr., 5 c.c. of the solution yielded 0·16 g. of the unchanged peroxide, m. p. and mixed m. p. 75—78°. (Kharasch, Fono, and Nudenberg[15] imply that reduction should have occurred by this stage; no reaction in fact takes place until alcohol is added. Their method of analysis of the products of the reaction of 1-methyl-1-phenylethyl 1-phenylethyl peroxide would apparently not distinguish between acetophenone and 1-phenylethanol.) Excess of 96% ethanol was added to the remainder of the mixture to dissolve the sodium. The product was poured on ice–water, and the ethereal layer washed and dried, yielding an oily solid. This was washed with light petroleum leaving impure triphenylmethanol (1·55 g.), m. p. 152—155°, mixed m. p. 155—157°. From the washings, acetophenone (0·3 g.) was recovered, b. p. 100°/17 mm. (semicarbazone, m. p. and mixed m. p. 202°).

(ii) *With sodium and methanol*. Methanol was added slowly to a solution of the peroxide (4·0 g.) in ether (50 c.c.) over sodium powder (1·6 g.). The ether was evaporated off and the residue distilled in steam. From the distillate, acetophenone (0·39 g.) was recovered. b. p. 84—88°/10 mm. (semicarbazone, m. p. 202°). The residue from the steam-distillation was impure triphenylmethanol (2·1 g.), m. p. 154—156°.

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