**835.*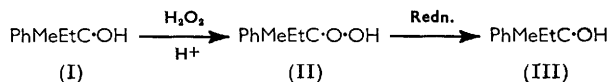* *Organic Peroxides. Part XI.*[1] *The Stereochemistry of the Reaction of Optically Active 2-Phenylbutan-2-ol with Hydrogen Peroxide.*

By Alwyn G. Davies.

Optically active 2-phenylbutan-2-ol has been reported to react with 30% hydrogen peroxide to give the corresponding hydroperoxide with almost complete inversion of configuration. We find, in contrast, that the reaction proceeds with almost complete racemisation.

OPTICALLY active 2-phenylbutan-2-ol (I) reacts with hydrogen peroxide to give the corresponding hydroperoxide (II), which can then be reduced back to the alcohol (III). The reduction (II $\longrightarrow$ III) proceeds with complete retention of configuration;[2] the ratio of

$$\text{PhMeEtC·OH} \xrightarrow[\text{H}^+]{\text{H}_2\text{O}_2} \text{PhMeEtC·O·OH} \xrightarrow{\text{Redn.}} \text{PhMeEtC·OH}$$
$$\quad\text{(I)} \qquad\qquad\qquad \text{(II)} \qquad\qquad\qquad \text{(III)}$$

the optical rotatory power of the initial and the final alcohol (α_{III}/α_{I}) thus gives in sign and magnitude a measure of the stereochemical course of the oxidation (I) $\longrightarrow$ (II).

[1] Part X, Davies and Packer, *J.*, 1961, 4390.
[2] Davies, *J.*, 1958, 3474.

In 1958 we showed [2] that in the reaction with 90% hydrogen peroxide in the presence of a trace of sulphuric acid, the value of α_{III}/α_I was between $+0.015$ and $+0.044$, *i.e.*, the oxidation occurred with retention of configuration accompanied by extensive racemisation. Experiments with the ^{18}O-labelled alcohol showed that the oxidation proceeded by alkyl–oxygen fission,[2,3] and, on the basis of a comparison of the reactivity of other alcohols,[4] it was proposed that the hydrogen peroxide reacted by an S_N1 process accompanied by a small S_Ni component.[2,5]

A similar study, but with 30% hydrogen peroxide, has recently been published by Choe and Tsutsumi.[6] Under these conditions oxidation of the alcohol is incomplete, and the hydroperoxide was extracted as its sodium salt with 10% sodium hydroxide. They found in two experiments that $\alpha_{III}/\alpha_I = -0.88$ and -0.90, respectively, *i.e.*, that the oxidation occurs with inversion of configuration accompanied by very little racemisation. Choe and Tsutsumi point out the contrast between their results and ours, and suggest that it may be due to the different concentration of the hydrogen peroxide used in the two sets of experiments.

They conclude that, under their conditions, the reaction follows an S_N2 mechanism, probably because the large alkyl groups sterically inhibit the solvation of the hydroxyl group which is necessary for an S_N1 reaction to proceed. It is more commonly believed that tertiary benzyl derivatives ArRR′CX usually react by an S_N1 mechanism, because of inductive and conjugative electron-release by the alkyl and the aryl group.[7] Such a reaction would be expected to involve substantial racemisation: we found that (−)-2-phenylbutan-2-ol reacted with sodium toluene-*p*-sulphinate to give the (±)-sulphone,[8] and Zeiss reported that the hydrogen phthalate underwent methanolysis with predominating racemisation accompanied by a small degree of inversion.[9]

We have now attempted to clarify this situation by repeating the reaction under Choe and Tsutsumi's conditions. The (+)-alcohol reacted with 30% hydrogen peroxide in the presence of sulphuric acid to give the hydroperoxide which was isolated in 24% yield and with a negligibly small rotation; from our previous value [2] of α_{III}/α_{II} it can be calculated that the oxidation (I) $\longrightarrow$ (II) has given racemisation accompanied by not greater than 3% of retention of configuration. This is similar to our results with 90% hydrogen peroxide [2] and is in direct contrast to Choe and Tsutsumi's report of almost complete inversion of configuration. The results are summarised in the Table.

Ref.	Concn. of H$_2$O$_2$ (%)	α_I	α_{II}	α_{II}/α_I	α_{III}/α_I
2	90	$+6.00°$	$+0.61°$	$+0.10$	$+0.038$
		$+6.24$	$+0.26$	$+0.04$	$+0.015$
5 *	30	$+14.00$	-29.32	-2.09	-0.88
		-19.10	$+38.22$	-2.01	-0.90
Present work	30	$+0.73$	$+0.02$	$+0.03$	$+0.01$ †

    * Choe and Tsutsumi quote specific rotations for solutions in ethanol, whereas our values are the measured rotations ($l = 1$) for the neat liquids. These two functions are very similar for the alcohol, $\alpha_D +13.77°$ corresponding to $[\alpha]_D +14.00°$ (in EtOH), and are probably also close for the hydroperoxide. The values for $[\alpha]_{III}/[\alpha]_I$ and α_{III}/α_I, of course, remain strictly comparable. Choe and Tsutsumi's value for $[\alpha]_{III}/[\alpha]_{II}$ ($+0.44$) is close to ours for α_{III}/α_{II} ($+0.37$), as would be expected.

    † Derived from $\alpha_{II}/\alpha_I \times \alpha_{III}/\alpha_{II}$, with α_{III}/α_{II} taken as $+0.37$.[2]

This irreproducibility is far outside any possible experimental error and appears to imply that under ostensibly similar conditions the oxidation can follow either of two

[3] Bassey, Bunton, Davies, Lewis, and Llewellyn, *J.*, 1955, 2471.
[4] Davies, Foster, and White, *J.*, 1953, 1541; 1954, 2200.
[5] Cf. Davies and Feld, *J.*, 1956, 655, 4669; 1958, 4637.
[6] Choe and Tsutsumi, *Nippon Kagaku Zasshi*, 1960, **81**, 586; *Chem. Abs.*, 1962, **56**, 397.
[7] *E.g.*, Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, Chap. 7, esp. pp. 324 and 325; Davies and Kenyon, *Quart. Rev.*, 1956, **9**, 203.
[8] Davies, Kenyon, and Salamé, *J.*, 1957, 3148.
[9] Zeiss, *J. Amer. Chem. Soc.*, 1953, **75**, 3154.

fundamentally different mechanisms. It is difficult to see however, what mechanism could result in inversion of configuration in this system, or to understand what the factors are that determine which of the two paths shall be followed.

EXPERIMENTAL

Optical rotations were measured visually on a Hilger mark III standard polarimeter; the readings are reproducible to about $\pm 0.02°$. The values for α_D quoted are for the neat liquids in 1 dm. tubes at 22—25°.

Reactions of (+)-*2-Phenylbutan-2-ol with* 30% *Hydrogen Peroxide.*—The alcohol (2·5 g.), $\alpha_D^{25} +0.73°$, available from our previous experiments,[2,8] was added to a mixture of 30% hydrogen peroxide (" AnalaR "; 10 c.c.) and concentrated sulphuric acid (0·05 c.c.) at 0°. The mixture was shaken, allowed to warm to room temperature, and then kept, without being stirred, in a thermostat at 30° for 20 hr. Water was then added and the organic layer was extracted into ether.

An attempt was made to separate the hydroperoxide by Choe and Tsutsumi's procedure. The ethereal solution (A) was extracted five times at 0° with a total of 50 c.c. of sodium hydroxide solution (1 : 9 w/w). When the aqueous extract was acidified with 4N-hydrochloric acid, there was no obvious separation of an oil, and less than 0·1 g. could be extracted into ether. This differs from Choe and Tsutsumi's report but is in accord with our previous experience.

The ethereal solution (A) was therefore evaporated, leaving an oily mixture of alcohol and hydroperoxide (38% by iodometric analysis [10]). This oil was mixed with an equal volume of light petroleum (b. p. 40—60°) and stirred with sodium hydroxide solution (45 : 55 w/w) at 0°; after 2 min. the solid sodium salt of the hydroperoxide separated.* This was filtered off and washed five times by suspending it in light petroleum and centrifuging out the salt. The light petroleum solutions were combined (B).

The salt was suspended in water and the hydroperoxide was liberated with carbon dioxide and extracted with light petroleum, yielding 1-methyl-1-phenylpropyl hydroperoxide (0·538 g.), b. p. 80—88° (bath)/0·01—0·02 mm., n_D^{25} 1·5197, $\alpha_D +0.02°$ (neat), $< +0.02°$ (c 24·6 in ethanol) (Found: peroxidic-O, 18·5. Calc. for $C_{10}H_{14}O_2$: peroxidic-O, 19·2%).

From the light petroleum solution (B), 2-phenylbutan-2-ol was recovered (0·708 g.) with b. p. 125° (bath)/16 mm., n_D^{25} 1·5162, $\alpha_D +0.69°$.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, GOWER STREET,
LONDON, W.C.1.

* In our earlier work,[2] although the experimental details were not given, a specimen of the hydroperoxide obtained from the alcohol was subjected to this procedure and recovered with undiminished rotation. This shows that the optical activity of the hydroperoxide was not in that work due to contamination by the active alcohol, and it establishes the validity of the procedure in the present experiments.

[10] Kokatnur and Jelling, *J. Amer. Chem. Soc.*, 1941, **63**, 1432.