934. *Organic Peroxides. Part IX.*[1] *A Stereochemical Study of the Formation of Alkyl Hydroperoxides from Hydrogen Peroxide.*

By Alwyn G. Davies and R. Feld.

Several optically active alkyl hydroperoxides (II) have been prepared by the reaction of hydrogen peroxide with the corresponding active alcohols (I) or their derivatives (Ia). Reduction of the hydroperoxide (II) back to the alcohol (III) permits conclusions to be drawn about the stereochemistry of the primary reaction.

In Parts VI [2] and VIII [1] we reported a stereochemical study of the formation and reduction of 1-phenylethyl hydroperoxide and of 1-methyl-1-phenylpropyl hydroperoxide respectively. Similar methods, illustrated in the scheme below, have now been applied to the investigation of a number of other hydroperoxides.

By the reaction of hydrogen peroxide with optically active 1-phenylethyl ether, 1-phenylpropanol, 1-phenylbutanol, 1-2′-naphthylethanol, 3-methylhexan-3-ol, 4-chlorodiphenylmethanol, and 2-1′-naphthylbutan-2-ol and its hydrogen phthalate, the corresponding optically active hydroperoxides have been prepared and characterised by their triphenylmethyl and/or 9-xanthenyl derivatives. The hydroperoxides from the first five compounds have been configurationally related to the corresponding alcohol by reduction. These results, and our previous ones, are summarised in Table 1.

Column 2 records the ratio of the rotatory power of the alcohol (III) to that of the hydroperoxide (II) from which it was obtained on reduction; where a number of reductions have been carried out, a mean value of α_{III}/α_{II} is recorded, the individual values appearing in the Experimental section.

If we assume that the reduction proceeds without affecting the asymmetric centre of the molecule,[1, 2] the factor in column 2 also represents in sign and magnitude the ratio of the

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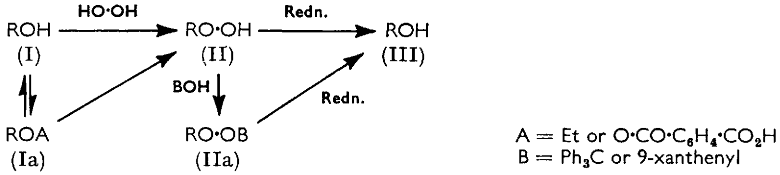
[1] Part VIII, Davies, *J.*, 1958, 3474.
[2] Davies and Feld, *J.*, 1956, 665.

rotations of the optically pure alcohol and hydroperoxide of like configuration. The maximum rotatory power of the alcohol (column 3) divided by this factor then gives an approximate value for the rotatory power of the optically pure hydroperoxide (column 4).

Column 5 records the percentage of activity remaining in the alcohol after the cycle alcohol (I) → hydroperoxide (II) → alcohol (III) (*i.e.*, $\alpha_{II}/\alpha_{I} \times \alpha_{III}/\alpha_{II}$). Again, the reduction (II) → (III) being assumed not to involve configurational change, this factor in column 5 represents in sign and magnitude the percentage configurational retention in the reaction (I) → (II). This factor will be minimal because no allowance has been made for the racemisation of the reactant or product.

When the reactant is a derivative of an alcohol (*i.e.*, ether or ester), the equivalent factor for the reaction is given by the expression $\alpha_{II}/\alpha_{Ia} \times \alpha_{Ia}/\alpha_{I} \times \alpha_{III}/\alpha_{II}$, where α_{Ia}/α_{I} is derived from an interconversion between (I) and (Ia) which proceeds with configurational retention.



A = Et or O·CO·C_6H_4·CO_2H
B = Ph_3C or 9-xanthenyl

In all the structural systems studied, the alcohol and its corresponding hydroperoxide and triphenylmethyl and 9-xanthenyl derivatives which have similar configurations have the same sign of rotation. The active hydroperoxides which we have prepared all have rotatory powers appreciably greater than those of the corresponding alcohols, but the reverse applies to Williams and Mosher's 1-methylhexyl hydroperoxide[3] and Ikeda's 1 : 2 : 3 : 4-tetrahydro-1-naphthyl hydroperoxide (Table). Both the magnitude and even the sign of rotation, however, may of course change as the solvent and wavelength are varied.

1 I or Ia	2 α_{III}/α_{II}	3 Max. α_{III}	4 Max. α_{II}	5 α_{III}/α_{I} (%)
Ph·CHMe·OH	+0·3$_0$ [a]	44·2° [b]	140° [a]	−3 [a]
Ph·CHMe·OEt				≮ −10
Ph·CHEt·OH	+0·2$_5$	27·8 [c]	120	−3
Ph·CHPr·OH	+0·5$_5$	51·4 [d] *	95	+5
2-$C_{10}H_7$·CHMe·OH	+0·7$_5$	55·8 [e] *	75	+7
Pr·CMeEt·OH	+0·2$_5$	— [f]	—	≯ ±5
Ph·CMeEt·OH	+0·3$_5$	18·1 [f, g]	50	+3 [h]
Ph·CMeEt·O·CO·R′				+10 [h]
α-Tet. OH	—	32·7 [i]	20 [j]	— ≯ ±5 [j]
α-Tet. O·CO·R′				≯ ±1 [j]

Notes: R′ = *o*-C_6H_4·CO_2H. α-Tet. = 1 : 2 : 3 : 4-tetrahydro-1-naphthyl. Specific rotations (in chloroform unless otherwise stated) are marked *.

[a] Davies and Feld, *J.*, 1956, 665. [b] Downer and Kenyon, *J.*, 1939, 1156. [c] Pickard and Kenyon, *J.*, 1911, **99**, 45; Kenyon and Wotton, unpublished work. [d] Kenyon and Partridge, *J.*, 1936, 128; this paper, Experimental. [e] Collyer and Kenyon, *J.*, 1940, 676. [f] Davies, Kenyon, and Salamé, *J.*, 1957, 3148. [g] Zeiss, *J. Amer. Chem. Soc.*, 1951, **73**, 2391. [h] Davies, *J.*, 1958, 3474. [i] Davies and White, *J.*, 1952, 3300. *j* In benzene solution. By direct resolution; Ikeda, *Bull. Lib. Arts Coll. Wakayama Univ.*, 1954, **4**, 27.

1 : 2 : 3 : 4-Tetrahydro-1-naphthol and its hydrogen phthalate give the inactive hydroperoxide, and 1-phenylethanol and 1-phenylpropanol react with racemisation accompanied by inversion of configuration. These reactions probably proceed by an S_N1 mechanism as we have described earlier.[2, 4, 5] The reaction of ethyl 1-phenylethyl ether must proceed

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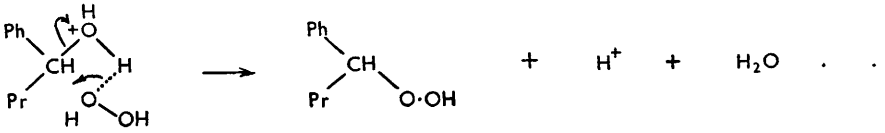
[3] Williams and Mosher, *J. Amer. Chem. Soc.*, 1954, **76**, 3495.
[4] (*a*) Davies, Foster, and White, *J.*, 1953, 1541; (*b*) *idem*, *J.*, 1954, 2200.
[5] Bassey, Bunton, Davies, Lewis, and Llewellyn, *J.*, 1955, 2471.

similarly (eqn. 1), although the reaction of phenyl 1-phenylethyl ether with hydrogen chloride has been shown to follow an $S_{\mathrm{N}}i$ mechanism.[6]

$$\mathrm{Ph{\cdot}CHMe{\cdot}OEt} \xrightarrow{\mathrm{H^+}} \mathrm{EtOH} + \mathrm{Ph{\cdot}\overset{+}{C}HMe} \xrightarrow{\mathrm{HO{\cdot}OH}} \mathrm{Ph{\cdot}CHMe{\cdot}O{\cdot}OH} + \mathrm{H^+} \quad . \quad . \quad . \quad . \quad (1)$$

1-Phenylbutanol, 1-2′-naphthylethanol, and 2-phenylbutan-2-ol and its hydrogen phthalate, however, give the corresponding hydroperoxides with predominating retention of configuration. Our experiments with ^{18}O-labelled reactants,[1, 5] supported by the general absence of reactions leading to the heterolytic formation of the O–O bond,[7] render it unlikely that these reactions follow a process other than one involving alkyl–oxygen fission. They therefore appear to proceed by an $S_{\mathrm{N}}i$ mechanism,[1] *e.g.*, eqn. (2).



(2)

EXPERIMENTAL

In experiments involving concentrated hydrogen peroxide, precautions were taken against explosion.

1-*Phenylethyl Compounds*.—The preparation and reduction of the active hydroperoxide and its triphenylmethyl and 9-xanthenyl derivatives, obtained from the active alcohol, are described in Part IV.[2]

Hydroperoxide from the ethyl ether. (−)-Ethyl 1-phenylethyl ether (0·75 g.), α_{D}^{18} −73·52° (*l* 1; undild.), was caused to react with hydrogen peroxide (8 c.c.) containing concentrated sulphuric acid (0·1 g.).[8] Impure 1-phenylethyl hydroperoxide (0·30 g.), b. p. 55—60°/0·01 mm., α_{D}^{18} −1·48° (*l* 0·25; undiluted), was isolated, but retained the characteristic odour of the ether. A fraction (0·2 g.) was therefore converted into the triphenylmethyl derivative (0·49 g.) which (uncrystallised) had m. p. 70—74°, mixed m. p. 73—77°, $[\alpha]_{\mathrm{D}}^{18}$ +7·28° (*l* 0·5; *c* 4·9 in $CHCl_3$), and after recrystallisation from ethanol, m. p. and mixed m. p. 80—81°.

In a second experiment the (+)-ether, α_{D}^{16} +12·12° (*l* 0·5; undiluted), after 12 hr. similarly gave a mixture of the hydroperoxide and unchanged ether, α_{D}^{22} +2·29° (*l* 0·5; undiluted), b. p. 50—56°/0·001 mm., which could not be separated by distillation. From this, the triphenylmethyl derivative was obtained in 70% yield, $[\alpha]_{\mathrm{D}}^{17}$ −1·87° (*l* 2; *c* 4·8 in $CHCl_3$), m. p. 79—81°, mixed m. p. with a pure sample with $[\alpha]_{\mathrm{D}}^{18}$ −1·35° (*l* 2; *c* 4·8 in $CHCl_3$), 78—80°.

These two experiments give values of $[\alpha]_{\mathrm{IIa}}/\alpha_{\mathrm{Ia}}$ of −0·099 and −0·154 respectively (mean −0·13); $\alpha_{\mathrm{Ia}}/\alpha_{\mathrm{I}} \geqslant +1{\cdot}68$;[9] $\alpha_{\mathrm{III}}/\alpha_{\mathrm{II}} = +0{\cdot}31$;[2] and $\alpha_{\mathrm{II}}/[\alpha]_{\mathrm{IIa}} = +1{\cdot}54$.[2]

Reduction of the hydroperoxide with triphenylphosphine. Triphenylphosphine (2·21 g.) in pentane was added dropwise to 1-phenylethyl hydroperoxide (1·16 g.), α_{D}^{25} −1·94° (*l* 1; undiluted), suspended in pentane; the solvent boiled under reflux, and triphenylphosphine oxide (m. p. 150°) separated.[10] The filtrate was washed with dilute aqueous hydrogen peroxide, and with water, and dried (K_2CO_3). Distillation gave 1-phenylethanol, b. p. 104°/16 mm., $n_{\mathrm{D}}^{25{\cdot}8}$ 1·5256, α_{D}^{19} −0·60 (*l* 1; undiluted), whence $\alpha_{\mathrm{III}}/\alpha_{\mathrm{II}} = +0{\cdot}31$.

The reduction of the hydroperoxide with phenylboronic acid had a value $\alpha_{\mathrm{III}}/\alpha_{\mathrm{II}} = +0{\cdot}34$.[11] These two values correlate well with the mean value of +0·31 which we have obtained previously with different reducing agents.[2]

1-*Phenylpropyl Compounds*.—*Hydroperoxide from the alcohol.* (±)-1-Phenylpropanol (3·0 g.) was added dropwise and with stirring to a mixture of 90% hydrogen peroxide (10 c.c.) and concentrated sulphuric acid (0·1 g.) at 0°. After 1 hr. the mixture was allowed to warm to room temperature and stirring was continued for a further 5 hr. Water (50 c.c.) was added and the organic layer extracted with ether, and the extract washed with saturated aqueous sodium

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[6] Hart and Eleuterio, *J. Amer. Chem. Soc.*, 1954, **76**, 1379.
[7] Bassey and Davies, unpublished work; M. Bassey, Thesis, London, 1958.
[8] Davies and Feld, *J.*, 1956, 4669.
[9] Phillips and Kenyon, *J.*, 1930, 1694; Hughes, Ingold, and Scott, *J.*, 1937, 1201.
[10] Cf. Horner and Jurgeleit, *Annalen*, 1955, **591**, 138.
[11] Davies and Moodie, *J.*, 1958, 2372.

hydrogen carbonate, and dried (Na_2SO_4). Distillation yielded 1-*phenylpropyl hydroperoxide* (2·43 g.), b. p. 52—54°/0·001 mm., n_D^{20} 1·5190 (Found: C, 71·2; H, 8·1. $C_9H_{12}O_2$ requires C, 71·0; H, 8·0%).

The (+)-alcohol (2·1 g.), α_D^{21} +10·84° (*l* 1; undiluted), similarly gave the (−)-hydroperoxide (1·89 g.), b. p. 64°/0·07 mm., n_D^{20} 1·5192, α_D^{21} −0·93° (*l* 1; undiluted), whence $\alpha_{II}/\alpha_I = -0{\cdot}086$.

From the (−)-alcohol (0·9 g.), α_D^{20} −12·15° (*l* 0·5; undiluted), the (+)-hydroperoxide (0·67 g.) was obtained, b. p. 54—56°/0·005 mm., α_D^{18} +1·51° (*l* 0·5; undiluted), whence $\alpha_{II}/\alpha_I = -0{\cdot}124$, giving a mean value of −0·10.

1-*Phenylpropyl triphenylmethyl peroxide.* The (±)-hydroperoxide (1·0 g.) in acetic acid (5 c.c.) was added to a solution of triphenylmethanol (1·98 g.) and concentrated sulphuric acid (1 drop) in acetic acid (10 c.c.). After 2 hr. the mixture was poured on crushed ice (50 c.c.) yielding a solid (2·03 g.) which was recrystallised four times from aqueous ethanol giving 1-*phenylpropyl triphenylmethyl peroxide*, m. p. 78° (Found: C, 85·2; H, 6·3. $C_{28}H_{26}O_2$ requires C, 85·2; H, 6·6%).

Similarly the (+)-hydroperoxide (0·34 g.), α_D^{18} +1·51° (*l* 0·5; undiluted), and triphenylmethanol (0·59 g.) gave the dialkyl peroxide (0·76 g.), m. p. 84—86°, $[\alpha]_D^{13}$ +2·01° (*l* 0·5; *c* 5·0 in $CHCl_3$).

1-*Phenylpropyl* 9-*xanthenyl peroxide.* (±)-1-Phenylpropyl hydroperoxide (0·20 g.) in acetic acid (3 c.c.) was added to xanthhydrol (0·26 g.) in acetic acid (5 c.c.). After 2 hr. the mixture was poured into water giving an oil which later solidified (0·29 g.). Four recrystallisations from ethanol gave 1-*phenylpropyl* 9-*xanthenyl peroxide*, m. p. 69—70° (Found: C, 79·1; H, 6·1. $C_{22}H_{20}O_3$ requires C, 79·5; H, 6·1%).

Reduction of the hydroperoxide with sodium sulphite. The hydroperoxide (1·50 g.), α_D^{21} −0·93° (*l* 1; undiluted), was shaken for 6 hr. with aqueous sodium sulphite (6·25 g. of the heptahydrate in 50 c.c. of water). An ethereal extract gave 1-phenylpropanol, b. p. 109—110°/15 mm., with a negative peroxide test, α_D^{19} −0·22° (*l* 1; undiluted), n_D^{20} 1·5224, whence $\alpha_{III}/\alpha_{II} = +0{\cdot}24$.

1-*Phenylbutyl Compounds.*—The optically pure alcohol, m. p. 49°, $[\alpha]_D^{18}$ −45·9° (in C_6H_6),[12] has $[\alpha]_D^{18}$ −51·4° (*l* 2; *c* 5·0 in $CHCl_3$). Optically impure alcohol may be liquid; the rotatory power of the undiluted alcohol is then related to that of its chloroform solution by the factor $[\alpha]_D$ (in $CHCl_3$)/α_D (*l* 1; undiluted) = +1·66.

Hydroperoxide from the alcohol. A mixture of 1-phenylbutanol (1·0 g.) and 90% hydrogen peroxide (5 c.c.) containing sulphuric acid (0·1 g.) was vigorously stirred for 10 hr., yielding 1-phenylbutyl hydroperoxide (0·52 g.), b. p. 62°/0·001 mm., n_D^{20} 1·5128, d_4^{20} 1·023. Ivanov, Savinova, and Zhakovskaya [13] prepared the same compound by autoxidation of butylbenzene and report b. p. 56°/0·006 mm., n_D^{20} 1·5103, d_4^{20} 1·016.

(+)-1-Phenylbutanol (6·0 g.), $[\alpha]_D^{20}$ +42·41° (*l* 1; *c* 10 in $CHCl_3$) was treated similarly, a little ether being added to increase the mutual solubility of the two phases. The (+)-hydroperoxide (4·4 g.) was isolated, b. p. 66°/0·1 mm., α_D^{21} +4·21° (*l* 1; undiluted) n_D^{20} 1·5120, d^{20} 1·020 (Found: C, 72·6; H, 8·6. $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·5%). A second preparation from the same alcohol gave the hydroperoxide, b. p. 66°/0·01 mm., α_D^{21} +2·04° (*l* 1; undiluted), n_D^{20} 1·5122. In the absence of sulphuric acid, no reaction occurred.

Likewise the (−)-alcohol (4·0 g.), $[\alpha]_D^{18}$ −51·4° (*l* 2; *c* 5·0 in $CHCl_3$), gave the (−)-hydroperoxide (3·80 g.), b. p. 58°/0·005 mm., n_D^{20} 1·5123, α_D^{18} −2·14° (*l* 0·5; undiluted). A second preparation from the same alcohol (1·75 g.) gave the hydroperoxide (1·20 g.), α_D^{17} −1·71° (*l* 0·5; undiluted). A third specimen of the alcohol (2·4 g.), $[\alpha]_D^{18}$ −50·0° (*l* 2; *c* 5·6 in $CHCl_3$) gave the hydroperoxide (1·97 g.), b. p. 59—61°/0·005 mm., n_D^{20} 1·5120, α_D^{20} −2·96° (*l* 1; undiluted).

These five experiments give values of $\alpha_{II}/[\alpha]_I$ of +0·099, +0·048, +0·083, +0·067, and +0·118 respectively (mean of +0·083).

1-*Phenylbutyl triphenylmethyl peroxide.* By the usual method, the hydroperoxide (0·20 g.) and triphenylmethanol (0·33 g.) gave 1-*phenylbutyl triphenylmethyl peroxide* (0·48 g., from aqueous ethanol), m. p. 55·5—57° (Found: C, 85·1; H, 7·1. $C_{29}H_{28}O_2$ requires C, 85·2; H, 6·9%).

The (−)-hydroperoxide (2·0 g.), α_D^{20} −2·96° (*l* 1; undiluted), similarly gave the (−)-dialkyl peroxide (4·2 g.), m. p. 55·5—57·5°, $[\alpha]_D^{17}$ −2·18° (*l* 2; *c* 5·03 in $CHCl_3$); the (−)-hydroperoxide, α_D^{17} −2·14° (*l* 0·5; undiluted), gave the crude dialkyl peroxide having $[\alpha]_D^{18}$ −3·08° (*l* 1; *c* 5·2 in $CHCl_3$), and after one recrystallisation, $[\alpha]_D^{18}$ −2·56° (*l* 1; *c* 4·7 in $CHCl_3$).

The differing values of $\alpha_{II}/[\alpha]_{IIa}$ for these two experiments indicate that fractionation of the

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[12] Kenyon and Partridge, *J.*, 1936, 128.

[13] Ivanov, Savinova, and Zhakovskaya, *Zhur. obshchei Khim.*, 1952, **22**, 781.

(−)- and (±)-dialkyl peroxide accompanies its isolation. In the reduction of this derivative (below), therefore, only the sign and not the magnitude of $\alpha_{\mathrm{III}}/[\alpha]_{\mathrm{IIa}}$ is significant.

1-*Phenylbutyl* 9-*xanthenyl peroxide.* A solution of the (±)-hydroperoxide (0·20 g.) and xanthhydrol (0·24 g.) in acetic acid (5 c.c.) yielded 1-*phenylbutyl* 9-*xanthenyl peroxide* (0·34 g., from aqueous ethanol), m. p. 68·5° (Found: C, 79·2; H, 6·3. $C_{23}H_{22}O_3$ requires C, 79·7; H, 6·4%).

The (+)-hydroperoxide (0·50 g.), α_{D}^{21} +2·04° (*l* 1; undiluted), gave the (+)-dialkyl peroxide (0·94 g.), m. p. 59—63°, $[\alpha]_{\mathrm{D}}^{22}$ +3·13° (*l* 0·5; *c* 6·2 in C_6H_6). Crystllisation from aqueous ethanol gave two fractions: (i) less soluble, m. p. 65°, $[\alpha]_{\mathrm{D}}^{19}$ +2·32° (*l* 0·5; *c* 5·4 in C_6H_6), and (ii) more soluble, m. p. 61—65°, $[\alpha]_{\mathrm{D}}^{18}$ +4·5° (*l* 0·5; *c* 4·9 in C_6H_6).

Reduction of the hydroperoxide. (i) *With sodium sulphite.* The (±)-hydroperoxide (1·0 g.) was shaken with aqueous sodium sulphite (4·5 g. of the heptahydrate in 36 c.c. of water) for 6 hr., yielding 1-phenylbutanol, b. p. 121°/21 mm., hydrogen phthalate, m. p. 89—91°.

The (−)-hydroperoxide (0·90 g.), α_{D}^{17} −1·71° (*l* 0·5; undild.), was treated similarly, but the mixture was shaken for 12 hr. to ensure complete reaction. The (−)-alcohol was isolated (0·46 g.), b. p. 122°/20 mm., n_{D}^{20} 1·5178, α_{D}^{18} −0·58° (*l* 0·5; undiluted), equivalent to $[\alpha]_{\mathrm{D}}^{18}$ −1·92° (in $CHCl_3$).

(ii) *With zinc and acetic acid.* Water (1 c.c.) and zinc (1·0 g.) were added to a solution of the (−)-hydroperoxide (1·0 g.), α_{D}^{17} −2·14° (*l* 0·5; undiluted), in acetic acid (5 c.c.). The mixture was warmed to 50°, whereupon the temperature rose spontaneously to 75°. After cooling, the filtrate from the mixture was made just acidic by the successive addition of sodium hydroxide and hydrochloric acid. An ethereal extract gave the (−)-alcohol (0·76 g.), α_{D}^{20} −0·68° (*l* 0·5; undiluted), equivalent to $[\alpha]_{\mathrm{D}}$ −2·26° (in $CHCl_3$), b. p. 118°/20 mm., n_{D}^{20} 1·5176.

The above two experiments gave values of $[\alpha]_{\mathrm{III}}/\alpha_{\mathrm{II}}$ of +0·56 and +0·53 respectively (mean +0·55).

(iii) *With lithium aluminium hydride.* The (±)-hydroperoxide (0·40 g.) was reduced with lithium aluminium hydride (0·11 g.) as for 1-phenylethyl hydroperoxide,[2] yielding an oil (0·20 g.). Treatment of this with phthalic anhydride (0·2 g.) and pyridine (1·2 g.) for 5 hr. at 60° gave 1-phenylbutyl hydrogen phthalate (from carbon disulphide–light petroleum), m. p. and mixed m. p. 91°.

Reduction of 1-*phenylbutyl triphenylmethyl peroxide with zinc and acetic acid.* The (−)-peroxide (4·0 g.), $[\alpha]_{\mathrm{D}}^{17}$ −2·18° (*l* 1; *c* 5·03 in $CHCl_3$), dissolved on warming in a mixture of acetic acid (40 c.c.) and water (5 c.c.). Zinc dust (5·0 g.) was added and the mixture kept at 80° for 30 min. (−)-1-Phenylbutanol (1·02 g.), b. p. 110°/15 mm., α_{D}^{17} −0·82° (*l* 1; undiluted), and triphenylmethanol (2·43 g.), m. p. 158—160°, were isolated.

A similar reduction of the specimen of the dialkyl peroxide (2·9 g.), $[\alpha]_{\mathrm{D}}^{18}$ −2·56° (*l* 1; *c* 4·7 in $CHCl_3$) (see above), gave (−)-1-phenylbutanol (0·48 g.), b. p. 112°/16 mm., α_{D}^{20} −0·98° (*l* 1; undiluted), n_{D}^{20} 1·5181.

$[\alpha]_{\mathrm{III}}/\alpha_{\mathrm{II}}$ Derived from $[\alpha]_{\mathrm{III}}/[\alpha]_{\mathrm{IIa}} \times [\alpha]_{\mathrm{IIa}}/\alpha_{\mathrm{II}}$ is therefore positive, *i.e.*, the same stereochemical effect predominates in the sequence (II) ⟶ (IIa) ⟶ (III) as in the direct reduction (II) ⟶ (III).

1-2′-*Naphthylethyl Compounds.—The hydroperoxide.* (i) *From the alcohol.* (−)-1-2′-Naphthylethanol (3·0 g.), $[\alpha]_{\mathrm{D}}^{17}$ −48·9° (*l* 1; *c* 4·8 in $CHCl_3$), was added with stirring to 90% hydrogen peroxide (10 c.c.) containing sulphuric acid (0·1 g.) at 0°. After 4 hours' stirring at room temperature a yellow oil (2·76 g.) was isolated which solidified after 1 week at 0°. Recrystallisation from a large volume of light petroleum gave (−)-1-2′-*naphthylethyl hydroperoxide*, m. p. 37—38°, $[\alpha]_{\mathrm{D}}^{18}$ −3·34° (*l* 1; *c* 4·8 in $CHCl_3$) (Found: C, 76·8; H, 6·5. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%).

A second preparation gave the (−)-hydroperoxide [0·60 g. from 1·0 g. of the same (−)-alcohol], m. p. 36—38°, $[\alpha]_{\mathrm{D}}^{19}$ −5·94° (*l* 1; *c* 5·2 in $CHCl_3$).

The above two experiments give values of $[\alpha]_{\mathrm{II}}/[\alpha]_{\mathrm{I}}$ of +0·068 and +0·121 respectively (mean +0·095).

(ii) *From the hydrogen phthalate.* The hydrogen phthalate (0·75 g.) was dissolved in 90% hydrogen peroxide (5 c.c.) containing sodium hydrogen carbonate (0·70 g.). After 12 hr. at 0° and 84 hr. at room temperature the initially clear solution was turbid. An ethereal extract of the diluted reaction mixture gave a solid (0·1 g.), m. p. 34—37°, mixed m. p. with the hydroperoxide from (i), 35—37°. Some hydrogen phthalate (0·52 g.), m. p. 90—91°, was recovered when the aqueous layer was acidified.

1-2'-*Naphthylethyl* 9-*xanthenyl peroxide.* By the usual method the (−)-hydroperoxide (60 mg.) gave 1-2'-*naphthylethyl* 9-*xanthenyl peroxide* (from ethanol, 90 mg.), m. p. 100° (Found: C, 81·1; H, 5·3. $C_{25}H_{20}O_3$ requires C, 81·5; H, 5·5%). The optical rotation was not measured.

An attempt to prepare the triphenylmethyl derivative gave an oil which could not be caused to solidify.

Reduction of the hydroperoxide with zinc and acetic acid. Zinc (1·0 g.) was added to a solution of the (−)-hydroperoxide (0·60 g.), $[\alpha]_D^{19}$ −5·94° (*l* 1; *c* 5·2 in $CHCl_3$), in 85% acetic acid (25 c.c.). The mixture was warmed to 60° and then allowed to cool. After 2 hr. the mixture was filtered into water and steam-distilled, giving 1-2'-naphthylethanol (0·23 g.), m. p. 65—67°, $[\alpha]_D^{19}$ −4·42° (*l* 1; *c* 4·5 in $CHCl_3$), whence $[\alpha]_{III}/[\alpha]_{II} = +0{\cdot}75$.

4-*Chlorodiphenylmethyl Compounds.—Hydroperoxide from the alcohol.* 4-Chlorodiphenylmethanol (0·5 g.) was added to 90% hydrogen peroxide (5 c.c.) containing concentrated sulphuric acid (0·1 g.) at 0°. The mixture was stirred at room temperature for 6 hr. and the crude hydroperoxide isolated as an oil (0·34 g.) which gave a strong peroxide test and could not be caused to solidify or distilled below 100°/0·001 mm.

A second preparation from the (+)-alcohol (2·0 g.), $[\alpha]_D^{18}$ +9·10° (*l* 1; *c* 5·0 in $CHCl_3$), similarly gave an intractable oil; its rotatory power was not measured.

Attempts were also made to prepare the hydroperoxide by solvolysis of the hydrogen phthalate in 90% hydrogen peroxide containing sodium hydrogen carbonate. Such solutions, however, are unstable and inflame about 3 hr. after preparation. If the solutions were diluted with water when this violent stage appeared imminent, the hydrogen phthalate could be recovered in 80% yield.

4-*Chlorodiphenylmethyl triphenylmethyl peroxide.* By the usual method the crude active hydroperoxide (0·50 g.) and triphenylmethanol (0·55 g.) gave a solid (0·81 g.), $[\alpha]_D^{21}$ −4·8° (*l* 2; *c* 2·8 in $CHCl_3$), m. p. 122—124°, which was recrystallised from ethanol giving 4-*chlorodiphenylmethyl triphenylmethyl peroxide*, m. p. 129° (Found: C, 80·5; H, 4·9; Cl, 6·7. $C_{32}H_{25}O_2Cl$ requires C, 80·6; H, 5·3; Cl, 7·4%).

A second sample of the crude hydroperoxide (0·70 g.) prepared from the same active alcohol (1·0 g.) gave the triphenylmethyl derivative (1·26 g.), m. p. 121—124°, $[\alpha]_D^{18}$ −0·4° (*l* 1; *c* 4·9 in $CHCl_3$).

1-*Ethyl*-1-*methylbutyl Compounds.—Hydroperoxide from the alcohol.* The alcohol (0·73 g.), α_D^{16} −0·36° (*l* 1; undiluted[14]), n_D^{20} 1·4225, gave 1-ethyl-1-methylbutyl hydroperoxide [4b] (0·54 g.), b. p. 40—41°/0·5 mm., n_D^{25} 1·4267, α_D^{19} +0·08° (*l* 1; undiluted).

In a second experiment the alcohol (0·54 g.), n_D^{20} 1·4224, b. p. 58—59°/25 mm., α_D^{19} +0·20° (*l* 1; undild.), yielded the hydroperoxide (0·34 g.), b. p. 38°/0·1 mm., n_D^{25} 1·4269, α_D^{19} 0·00° (*l* 0·5; undiluted), and the hydrogen perphthalate,[4b] m. p. 90°, mixed m. p. 90—92°, $[\alpha]_D^{19}$ 0·00° (*l* 1; *c* 10 in EtOH and in $CHCl_3$).

Reduction of the hydroperoxide with sodium sulphite. The (+)-hydroperoxide (0·54 g.), α_D^{19} +0·08°, was reduced by shaking it for 17 hr. with a solution of sodium sulphite (3·8 g.) in water (7 c.c.). The alcohol was recovered, b. p. 62°/*ca.* 25 mm., n_D^{25} 1·4197, $[\alpha]_D^{19}$ 0·0° (*l* 0·5; *c* 50 in EtOH).

1-*Methyl*-1-1'-*naphthylpropyl Compounds.—Hydroperoxide from the alcohol.* The alcohol [15] (1·0 g.) in ether (1 c.c.) was added dropwise with stirring at 0° to 90% hydrogen peroxide (7 c.c.) containing concentrated sulphuric acid (0·05 c.c.). The mixture was allowed to warm to room temperature, and stirring was continued for a further 3 hr. The hydroperoxide was isolated as a yellow oil, b. p. >100°/0·001 mm., which could not be caused to solidify.

Hydroperoxide from the hydrogen phthalate. A solution of the hydrogen phthalate (0·75 g.) in 90% hydrogen peroxide (7 c.c.) containing sodium hydrogen carbonate (0·8 g.) was kept at 0° for 96 hr. Dilution with water (50 c.c.) gave the hydroperoxide (0·33 g.) as a yellow oil. On acidification of the aqueous layer, some of the hydrogen phthalate (0·17 g.) was recovered.

In a similar experiment the (+)-hydrogen phthalate (0·92 g.), $[\alpha]_D$ +51·6° (*l* 2; *c* 4·0 in EtOH), yielded the hydroperoxide, $[\alpha]_D^{16}$ −6·33° (*l* 0·5; *c* 5·9 in $CHCl_3$).

Solutions of the sodium alkyl phthalate in hydrogen peroxide are unstable at room temperature and inflame after about 3 hr.

1-*Methyl*-1-1'-*naphthylpropyl triphenylmethyl peroxide.* The crude (±)-hydroperoxide (0·21

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[14] Davies, Kenyon, and Salamé, *J.*, 1957, 3148.

[15] Davies, Kenyon, and Thaker, *J.*, 1957, 3151.

g.) gave the (±)-*triphenylmethyl derivative* (0·44 g., from aqueous methanol), m. p. 114° (Found: C, 86·4; H, 6·6. $C_{33}H_{30}O_2$ requires C, 86·4; H, 6·6%).

Similarly the (−)-hydroperoxide (0·29 g.), $[\alpha]_D^{16}$ −6·33° (*l* 0·5; *c* 5·9 in $CHCl_3$), gave the (−)-triphenylmethyl derivative (0·35 g.), m. p. 107—112°, $[\alpha]_D^{17}$ −6·28° (*l* 0·5; *c* 3·5 in $CHCl_3$) before crystallisation.

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CHEMISTRY DEPARTMENT, BATTERSEA COLLEGE OF TECHNOLOGY,
LONDON, S.W.11.
WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1.

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