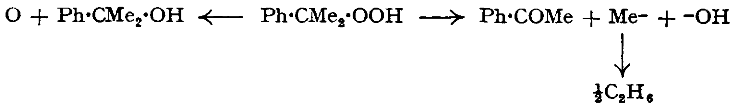
# **446.** *Reactions of Organic Peroxides. Part II. Reactions of αα-Dimethylbenzyl Hydroperoxide ("* iso*Propylbenzene Hydroperoxide").*

By E. G. E. Hawkins.

Decomposition of αα-dimethylbenzyl hydroperoxide by ferrous sulphate, under the influence of various catalysts and thermally, gives rise to mixtures of 2-phenylpropan-2-ol, acetophenone, and α-methylstyrene. Oxidation with permanganate and the reaction with Grignard compounds have been studied. Oxidation of olefins, *iso*propanol, aldehydes, and ketones by the hydroperoxide has been carried out.

It was first shown by Hock and Lang (*Ber.*, 1944, **77**, 257) that oxidation of *iso*propylbenzene by air gives rise to a hydroperoxide, $Ph{\cdot}CMe_2{\cdot}OOH$, although high concentrations of this compound were not obtained by them. Methods of improving the conversion into hydroperoxide have since been developed (Armstrong, Hall, and Quin, B.P. 610,293, 630,286; *J.*, 1950, 666). Acid decomposition of the hydroperoxide to yield phenol and acetone, and reduction with sodium sulphite to provide 2-phenylpropan-2-ol, have also been described by Hock and Lang (*loc. cit.*).

It has now been found that on treatment with ferrous sulphate αα-dimethylbenzyl hydroperoxide is converted into a mixture of acetophenone and 2-phenylpropan-2-ol; a gas is evolved, containing a high percentage of ethane, presumably from the reaction in which acetophenone is produced. The ferrous sulphate is simultaneously oxidised to a ferric compound.



$$\begin{tikzcd}[column sep=small] \mathrm{O} + \mathrm{Ph{\cdot}CMe_2{\cdot}OH} & \mathrm{Ph{\cdot}CMe_2{\cdot}OOH} \arrow[l] \arrow[r] & \mathrm{Ph{\cdot}COMe} + \mathrm{Me}\text{-} \arrow[d] + \text{-}\mathrm{OH} \\ & & \tfrac{1}{2}\mathrm{C_2H_6} \end{tikzcd}$$

The ferrous sulphate decompositions of the hydroperoxides of *sec.*-butylbenzene (Part I, *J.*, **1949**, 2076) and di*iso*propylbenzene (unpublished) appear to proceed in a similar manner.

Catalytic decomposition of the hydroperoxide also yields mixtures of acetophenone and alcohol, with variable proportions of α-methylstyrene produced by dehydration of the latter. The relative quantities of these constituents and the speed of decomposition appear to vary with the catalyst used.

Thermal decomposition of the hydroperoxide, with and without solvent, gives rise to the same products as the catalytic reactions.

Oxidation of the hydroperoxide with aqueous permanganate appears to follow a rather involved course. Some benzoic acid is formed, but the major products are again those given by simple catalytic decomposition, *i.e.*, acetophenone and carbinol.

Reaction with methylmagnesium iodide is vigorous and the end product is entirely α-methylstyrene. Presumably the alcohol is the initial product of reaction, and dehydration is brought about by the presence of iodine formed during the reaction. Ethylmagnesium bromide yields almost entirely a mixture of 2-phenylpropan-2-ol and α-methylstyrene indicating that the Grignard reagents act in a reducing capacity.

The hydroperoxide may act as a mild oxidising agent towards olefins in the presence of catalysts ($V_2O_5$, $OsO_4$); thus *cyclo*hexene yields the epoxide and traces of adipic acid, as well as various alcoholic and ketonic compounds which were not investigated. In the presence of vanadium pentoxide oct-1-ene also gives a small quantity of epoxide. Allyl alcohol yields polymeric products.

Oxidation of other types of organic compounds, in addition to olefins, is possible in presence of catalysts. A secondary alcohol (*iso*propanol) is oxidised to the corresponding ketone (acetone) in the presence of a variety of catalysts; 2-phenylpropan-2-ol and acetophenone are simultaneously produced, the latter representing a loss with respect to the oxidation of *iso*propanol.

$$\mathrm{Ph{\cdot}CMe_2{\cdot}OOH} + \mathrm{Me_2CH{\cdot}OH} \longrightarrow \mathrm{Ph{\cdot}CMe_2{\cdot}OH} + \mathrm{Me_2CO}$$

Further, aldehydes may be oxidised to the corresponding acids. In this case the reaction may proceed without a catalyst, but its presence increases the speed of reaction and allows a lower temperature to be used. In this way acetaldehyde, butyraldehyde, 2-ethylhexanal, and benzaldehyde have been smoothly oxidised; the hydroperoxide is reduced to 2-phenylpropan-2-ol.

$$\mathrm{Ph{\cdot}CMe_2{\cdot}OOH} + \mathrm{R{\cdot}CHO} \longrightarrow \mathrm{Ph{\cdot}CMe_2{\cdot}OH} + \mathrm{R{\cdot}CO_2H}$$

Attempts to oxidise acraldehyde to acrylic acid under a variety of conditions led only to polymerisation, as might be expected in the presence of an excess of peroxide.

Aliphatic ketones appear not to be oxidised very readily. Methyl ethyl ketone is converted into diacetyl only to a small extent; attempts to increase the conversion led to spontaneous decomposition of the peroxide, possibly owing to acid formation from the ketone by carbon–carbon fission.

*cyclo*Hexanone is oxidised in much less than the stoicheiometric amount to adipic acid.

It is of interest to compare the above reactions of the hydroperoxide with those of *tert.*-butyl hydroperoxide and aldehydes or ketones where, in the presence of acidic catalysts, condensation products are formed (U.S.P. 2,455,569; Dickey, Rust, and Vaughan, *J. Amer. Chem. Soc.*, **1949**, **71**, 1432):

$$\mathrm{R{\cdot}CHO} + \mathrm{CMe_3{\cdot}OOH} \longrightarrow \mathrm{R{\cdot}CH(OH){\cdot}OO{\cdot}CMe_3}$$

$$\mathrm{R_2CO} + 2\mathrm{CMe_3{\cdot}OOH} \longrightarrow \mathrm{R_2C(OO{\cdot}CMe_3)_2} + \mathrm{H_2O}$$

## EXPERIMENTAL.

M. p.s are uncorrected, and elementary analyses are by Drs. Weiler and Strauss. Analyses of the peroxide decomposition products—2-phenylpropan-2-ol, acetophenone, and α-methylstyrene mixtures—were generally carried out by infra-red absorption spectroscopy by using the method of matching with synthetic mixtures (Philpotts and Thain, forthcoming publication).

2-*Phenylpropan*-2-*ol*.—For comparative purposes, and as a standard for infra-red analyses, a pure sample of the alcohol was prepared from acetophenone and methylmagnesium iodide in the normal manner. It had b. p. *ca.* 90°/15 mm. and, after three recrystallisations from light petroleum, m. p. 33—34° (Found: C, 79·4; H, 9·0. Calc. for $C_9H_{12}O$: C, 79·4; H, 8·8%).

*Reactions of* αα-*Dimethylbenzyl Hydroperoxide*.—*Ferrous sulphate*. Hydroperoxide (29·5 g.) and ferrous sulphate (45 g. in 100 c.c. of water) were shaken together; the mixture became warm. Gas was evolved; a portion, on analysis, was found to contain 72·5% of ethane. The product was worked up in the normal manner and finally distilled; the bulk of the distillate (13·5 g.) had b. p. 180—200°, and contained acetophenone (6·6 g.; identified by its 2 : 4-dinitrophenylhydrazone); infra-red analysis showed the remainder to be 2-phenylpropan-2-ol.

*Catalytic decomposition*. (i) Hydroperoxide (20 g.) in heptane (50 g.) containing a trace of vanadium pentoxide was heated at 110—120° for 16 hours before decomposition was complete. Distillation provided, apart from the heptane, material (17·2 g.), b. p. *ca.* 96°/25 mm., and a residue (1·7 g.). Infra-red analysis of the distillate showed it to consist of 2-phenylpropan-2-ol (55%), acetophenone (29%), and α-methylstyrene (13%).

(ii) Experiment (i) was repeated, but the vanadium pentoxide was replaced by osmium tetroxide (2 c.c. of a 1% solution in *tert.*-butanol). Decomposition was complete in 4 hours. Distillation provided heptane and a product (13·3 g.), b. p. 60—90°/20 mm., as well as a residue (1·8 g.). Infra-red analysis showed the distillate to contain acetophenone (11%) and α-methylstyrene (88%), but no carbinol.

(iii) Hydroperoxide (10 g.) and manganese naphthenate (0·1 g.) were heated on the water-bath for 6 hours; >90% of the peroxide had decomposed during the first 2 hours. Distillation yielded the product (8·5 g.), b. p. 90—100°/20—25 mm., and a residue (0·8 g.). The product contained carbinol (75%), acetophenone (19·5%), and α-methylstyrene (*ca.* 1%).

*Thermal decomposition*. (i) Hydroperoxide (10 g.) in *iso*propylbenzene (25 g.) was heated at 140—150° (bath-temp.) for 11 hours before complete decomposition occurred. The distillate (14·0 g.), b. p. 80—83°/15 mm., contained the propanol (73%), acetophenone (21%), and α-methylstyrene (0·7%).

(ii) Hydroperoxide (20 g.) was slowly dropped (1 hour) through a tube packed with broken porcelain and heated to 200—220°; the product passed through a condensing system. The collected material (17·5 g.) smelt strongly of formaldehyde. It was dissolved in light petroleum, and the solution dried and distilled to give fractions (1) (trace), b. p. <60°, (2) (13·0 g.), b. p. 185—195°, (3) (1·1 g.), b. p. 110—150°/15 mm., and a residue (1·2 g.).

Fraction 1 smelt strongly of formaldehyde, the presence of which was confirmed by formation of its 2 : 4-dinitrophenylhydrazone. Fraction 2 contained phenol (3·7%), and by infra-red analysis, the propanol (2%), acetophenone (70%), and α-methylstyrene (10%). Fraction 3 was similarly shown to contain mainly acetophenone, but also a little carbinol and α-methylstyrene.

*Oxidation*. Potassium permanganate (30 g.) in water (250 c.c.) was stirred at 30°, and hydroperoxide (20 g.) added dropwise. Manganese dioxide formed during the reaction was filtered off; the filtrate was acidified and extracted with ether. After removal of solvent the product on distillation gave fractions (1) (9·0 g.), b. p. 88—100°/15 mm., (2) (4·3 g.), b. p. 100—128°/15 mm., and a residue (1·2 g.). Fraction 1, according to infra-red analysis, contained the propanol (66%) and acetophenone (25·5%), but no α-methylstyrene. Fraction 2 contained the propanol (33·5%), acetophenone (41·7%), and benzoic acid (13·0%; crystals of this separated on storage).

*Methylmagnesium iodide*. Hydroperoxide (20 g.) was gradually added to the Grignard reagent from methyl iodide (60 g.). A vigorous reaction took place in which some iodine appeared to be liberated. The product was worked up in the normal way. Distillation led to some dehydration; the product (8·2 g.) had b. p. 145—155°, and left a residue (1·2 g.). The distillate contained some free iodine. Infra-red analysis showed the distillate to consist of α-methylstyrene (97%), with no appreciable quantity of carbinol or acetophenone.

*Ethylmagnesium bromide*. The reaction of hydroperoxide (20 g.) with the Grignard reagent from ethyl bromide (50 g.), carried out as above, yielded as product a mixture (14·8 g.) shown by infra-red analysis to consist almost entirely of 2-phenylpropan-2-ol (60%) and α-methylstyrene (32%).

cyclo*Hexene*. (i) Hydroperoxide (25 g.) and *cyclo*hexene (50 g.) containing a trace of vanadium pentoxide were heated on the water-bath for 2 hours, and then under reflux on an oil-bath for 17 hours before the peroxide had completely disappeared. Distillation yielded unchanged olefin and fractions, b. p. 90—150° (2·5 g.), b. p. 150—170° (7·4 g.), and b. p. 94—98°/16 mm. (19·0 g.), and a residue (2·9 g.). The last fraction was 2-phenylpropan-2-ol formed by reduction of the hydroperoxide (Found: Active H, 0·73%. Calc. for $C_9H_{12}O$: 0·74%). The first two fractions were combined and redistilled to yield mainly material (6·3 g.), b. p. 130—134°, $n_D^{20}$ 1·4543 (epoxide content, 94%, calc. as *cyclo*hexene epoxide; Nicolet and Poulter, *J. Amer. Chem. Soc.*, 1930, **52**, 1186). Treatment with warm dilute sulphuric acid, followed by extraction with ether, provided *cyclo*hexane-1 : 2-diol, m. p. 100—102°, undepressed on admixture with an authentic specimen.

(ii) Hydroperoxide (13 g.) in *cyclo*hexene (6·5 g.) was added gradually, with shaking, to *cyclo*hexene (13 g.) containing osmium tetroxide (1 c.c. of 0·5% solution). The reaction was exothermic and external cooling had to be applied. At the end of the addition no free peroxide remained and the solution was distilled. Only small quantities of oxidation products of *cyclo*hexene were formed; these distilled with the 2-phenylpropan-2-ol (from the hydroperoxide) and could not be easily separated from it. A *p*-nitrophenylhydrazone, m. p. 244—245° (decomp.), was isolated; its analysis agreed with that expected of a bis-derivative from a cyclic $C_6$-diketone (Found : C, 56·8; H, 4·9; N, 22·0. Calc. for $C_{18}H_{18}O_4N_6$ : C, 56·5; H, 4·7; N, 22·0%.

No epoxide was isolated in this experiment, but from the residue was obtained a trace of slightly impure adipic acid, m. p. 147—148° (mixed m. p. undepressed) (Found : equiv., 79. Calc. for $C_6H_{10}O_4$ : equiv., 73).

*Oct*-1-*ene*. Hydroperoxide (25 g.) and oct-1-ene (35 g.), containing a trace of vanadium pentoxide, were heated at *ca.* 120° for 11½ hours, decomposition of the peroxide being then complete. After removal of unchanged octene distillation at 22 mm. provided fractions boiling from 70° to 105°. These consisted mainly of 2-phenylpropan-2-ol, but contained 3·1 g. of epoxide (calc. as 1 : 2-epoxy-octane; Nicolet and Poulter, *loc. cit.*). The product was not further examined.

*Allyl alcohol*. (i) Hydroperoxide (30 g.) and allyl alcohol (20 g.) were heated on the water-bath for *ca.* 30 hours for complete disappearance of peroxide. Distillation yielded 2-phenylpropan-2-ol (24·5 g.), b. p. 94°/16 mm., and a residue of brown gummy resin (14·5 g.).

(ii) The same quantities as in (i) being used, the hydroperoxide was added gradually, with shaking and cooling, to the alcohol containing osmium tetroxide (0·2 c.c. of 0·5% solution). The reaction was complete at the end of the addition. Distillation again gave only the propanol (24·2 g.) and left a resin (11·0 g.).

iso*Propanol*. The hydroperoxide (20 g.) and *iso*propanol (30 g.) containing a trace of catalyst were heated to gentle ebullition (bath-temp. 120°). Liquid was allowed to distil off slowly through a short (1 ft.) packed column. Fresh *iso*propanol was added at the same rate as liquid distilled. Acetone produced was determined by titration of portions of the distillate, and the heating continued until the peroxide had completely decomposed. The *iso*propanol was then removed, and the residue distilled and analysed by the infra-red method; it was found to contain varying proportions of the propanol, acetophenone, and α-methylstyrene, but no phenol except when chromic oxide was used as catalyst (see following table).

| Catalyst. | Time (hrs.). | Acetone produced (g.). | Catalyst. | Time (hrs.). | Acetone produced (g.). |
|---|---|---|---|---|---|
| $V_2O_5$ .................. | 4½ | 2·84 | $CrO_3$ .................. | 8 | 5·05 * |
| $OsO_4$ .................. | — | 2·71 | $Al(OPr^i)_3$ ........... | 1 week | 3·53 |
| $MnO_2$ .................. | 16 | 3·83 | Mn naphthenate ... | 15 | 1·96 |
| $WO_3$ ..................... | 15 | 2·96 | Co naphthenate ... | 20 | 2·4 |

* Crude residue contained phenol, and presumably part of the acetone produced was due to slight acid decomposition of the peroxide.

*Acetaldehyde*. (i) Hydroperoxide (5 g.) was gradually added to acetaldehyde (6 g.) at $< -10°$. After 3 hours very little of the peroxide had reacted.

(ii) Acetaldehyde (12 g.) was slowly added to hydroperoxide (10 g.), containing a trace of osmium tetroxide solution, the mixture being cooled below −10°. After 3 hours the peroxide had completely reacted and titration indicated the presence of acetic acid (3·58 g., *ca.* 92%, calc. on the peroxide). Distillation gave acetic acid (3·49 g.) and a mixture of the propanol (60%), acetophenone (15%), and α-methylstyrene (25%).

*Butyraldehyde*. (i) Hydroperoxide (92·5%; 10 g.) was added slowly to butyraldehyde (8 g.) cooled below 0°. After ½ hour at room temperature very little reaction had taken place; the mixture was heated at 40—50° for ½ hour, then at 90—100° for 3½ hours, before complete peroxide decomposition had occurred. The butyric acid formed was 5·09 g. (by titration), *i.e.*, 95% calc. on peroxide. Distillation provided butyric acid (4·47 g.) and 2-phenylpropan-2-ol (free from acetophenone).

(ii) The experiment was repeated at 90—100° throughout. Reaction was complete in 3 hours. The yield of butyric acid (by titration) was 90%.

(iii) Hydroperoxide (20 g.) and butyraldehyde (13·9 g.), containing a trace of vanadium pentoxide, were heated at 110° for 3 hours. The butyric acid formed was 8·9 g. (77%; by titration). After removal of the acid by alkali the residue yielded a distillate (15 g.), b. p. 70—86°/15 mm., and a residue (1·3 g.), the former containing the propanol (85%) and acetophenone (13%), but no α-methylstyrene.

(iv) Hydroperoxide (10 g.) and butyraldehyde (8 g.) containing osmium tetroxide (1 c.c. of 1% solution) were allowed to react at 0° and then kept overnight at room temperature; the peroxide had completely reacted. Titration showed the presence of 3·84 g. of butyric acid; distillation yielded butyric acid (3·66 g.) and a fraction (7·9 g.) containing the propanol (77%) and acetophenone (14%), but no α-methylstyrene.

(v) Hydroperoxide (10 g.) was gradually added, with stirring, to a mixture of butyraldehyde (8 g.) and methanol (22 g.) containing osmium tetroxide (1 c.c.; 1% solution) at −10° to −15°. After being kept overnight at room temperature the solution was heated at 80° for 5 hours. Titration showed the presence of butyric acid (5·65 g., 97·6%).

2-*Ethylhexanal*. Hydroperoxide (10·6 g.) was gradually added to 2-ethylhexanal (12·0 g.) containing osmium tetroxide (1 c.c.; 1% solution), the temperature being kept below −10°. After 4 hours 10% of the hydroperoxide remained unchanged, but next morning the reaction was complete. The 2-ethylhexanoic acid formed (10·4 g.) yielded a *p*-bromophenacyl ester, m. p. 94—98°. After removal of the acid by alkali the residue contained the propanol (72%) and a mixture (15—20%) of acetophenone and ethylhexanal.

*Benzaldehyde.* Hydroperoxide (5 g.) was added to freshly distilled benzaldehyde (5 g.), containing osmium tetroxide, at 0°. Reaction was complete in 1½ hours; benzoic acid (4·65 g., 91%, calc. on peroxide) and a mixture of (mainly) the propanol and acetophenone were produced. Benzoic acid, m. p. 121°, was regenerated from the alkali washings of the reaction product.

*Acraldehyde.* Several attempts were made to oxidise acraldehyde with the hydroperoxide, using an osmium tetroxide catalyst and in the presence of various antipolymerisation catalysts, *e.g.*, sulphur, tannic acid, but in every case polymerisation set in during the course of the oxidation; the temperature became out of control at this point.

*Methyl ethyl ketone.* Hydroperoxide (30 g.) and methyl ethyl ketone (15 g.) were heated at a bath-temp. of *ca.* 100°. The solution gradually became slightly yellow, but after 7 hours it became black and a rapid decomposition had set in. Distillation provided unchanged ketone containing traces of diacetyl (gave nickel-dimethylglyoxime), but the higher-boiling material (b. p. *ca.* 180°; 11·3 g.) was phenol, which crystallised on storage. A black residue (9·5 g.) remained.

cyclo*Hexanone.* Hydroperoxide (10 g.) and *cyclo*hexanone (4 g.) were heated together for 2 hours at 100—110° but very little decomposition of the peroxide occurred. Copper naphthenate was added and heating continued for a further 7 hours before complete destruction of the peroxide occurred. Titration showed the presence of 1·2 g. of acid (as adipic acid). Unchanged *cyclo*hexanone (1·87 g.) and decomposition products of the peroxide (6·2 g.) were removed by distillation, and the residue was extracted with boiling water. A little adipic acid, m. p. 150°, undepressed on admixture with an authentic sample, crystallised from the aqueous extract.

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