

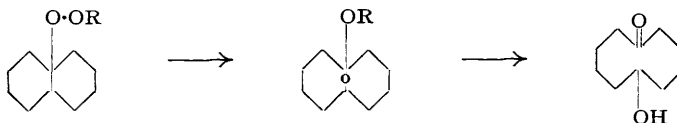
541. Reactions of Organic Peroxides. Part IV. Reactions of Methylcyclopentyl and Methylcyclohexyl Hydroperoxides.

By E. G. E. HAWKINS.

The decomposition of methylcyclopentyl hydroperoxide thermally and by reducing agents, acid, and alkali, as well as its condensation with ketones, have been studied. Many of the decomposition products are similar to those formed during the oxidation of methylcyclopentane (Part III). The corresponding reactions of methylcyclohexyl hydroperoxide lead to similar products.

VERY little attention appears to have been paid to the reactions of *cycloalkyl* hydroperoxides. Milas and Perry (*J. Amer. Chem. Soc.*, 1946, **68**, 1938) obtained the perphthalate from a 70% concentrate of methylcyclohexyl hydroperoxide, prepared by reaction of hydrogen peroxide with methylcyclohexyl hydrogen sulphate, and the same hydroperoxide has been produced by oxidation of methylcyclohexane itself by Ivanov and Savinova (*Doklady Akad. Nauk. S.S.R.*, 1948, **59**, 493) and reduced to the carbinol with zinc and acetic acid. The isolation of several substituted cyclic paraffin hydroperoxides from the products of aerial oxidation of the hydrocarbons has been claimed (Union Oil Co., U.S.P. 2,430,864, 2,430,865) but no reactions of these hydroperoxides have been described. It has recently been found (Criegee and Dietrich, *Annalen*, 1948, **560**, 135) that 1-methyl- and 1-ethyl-cyclohexyl hydroperoxides can be characterised by their crystalline *p*-nitrobenzoates.

Decalin 9-hydroperoxide on reduction yields *trans*-decal-9-ol (Criegee, *Ber.*, 1944, **77**, B, 22; Ivanov and Savinova, *Compt. rend. U.S.S.R.*, 1945, **48**, 31); the benzoate provides the same reduction product (Criegee, *loc. cit.*). It was also found by Criegee (*Ber.*, 1944, **77**, B, 722; *Annalen*, 1948, **560**, 127) that heating esters of decalin 9-hydroperoxide gave an isomeric hemiacetal, which on hydrolysis yielded 6-hydroxycyclodecan-1-one :



Chavanne *et al.* (for refs. see Part III, preceding paper) showed that oxidation of many alkylcycloalkanes gave ketones, alcohols, and keto-acids which very probably arose from decomposition of intermediate hydroperoxides. In the same way the many products formed from methylcyclopentane (Part III) probably arose from the hydroperoxides.

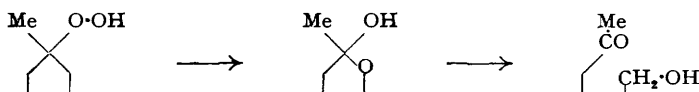
It has now been found that the decomposition products of methylcyclopentyl and methylcyclohexyl hydroperoxides can be explained by the reaction of free radicals, such as (I) and (II) which would be first formed from methylcyclopentyl hydroperoxide. Reduction of methylcyclopentyl hydroperoxide with sodium sulphite gives the expected carbinol, 1-methylcyclopentanol.



Thermal decomposition of both these hydroperoxides is slow (compared with that of phenylalkyl hydroperoxides) and gives a mixture of products, the majority ketonic. Thus

methylcyclopentyl hydroperoxide gives methyl butyl ketone, 1-methylcyclopentanol, 6-hydroxyhexan-2-one, traces of unsaturated and other ketones, and 5-ketohexanoic acid. Similarly methylcyclohexyl hydroperoxide gives mainly a mixture of methyl amyl ketone and 1-methylcyclohexanol.

Acid decomposition of methylcyclopentyl hydroperoxide provides mainly methyl butyl ketone and 6-hydroxyhexan-2-one, both derived from the same radical (II), one by gain of hydrogen and the other by gain of hydroxyl (see Part III). Alternatively the ketol may have arisen by a rearrangement similar to that of the decalin hydroperoxide esters :



Sodium hydroxide reacts vigorously with methylcyclopentyl hydroperoxide to yield methyl butyl ketone, 1-methylcyclopentanol, and acid decomposition products including pyruvic acid. Methylcyclohexyl hydroperoxide similarly yielded mainly a mixture of methyl amyl ketone and an alcohol (presumably 1-methylcyclohexanol).

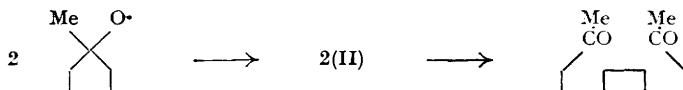
Sodium carbonate brings about a much slower decomposition of methylcyclopentyl hydroperoxide : the products again include methyl butyl ketone, but the main alcoholic constituent is 6-hydroxyhexan-2-one.

When methylcyclopentyl hydroperoxide is heated with butyraldehyde a somewhat complex reaction appears to take place. Some of the aldehyde is converted into acid but part probably condenses with the hydroperoxide. An attempt to distil the products led to rapid decomposition in which butyric acid and ketonic products were formed.

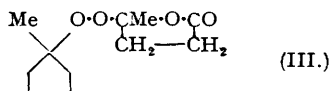
Acetone and methylcyclopentyl hydroperoxide condense in the presence of mineral acid to yield the expected 2 : 2-di-(1-methylcyclopentylperoxido)propane, which on pyrolysis gives



formaldehyde, methyl butyl ketone, and dodecane-2 : 11-dione. The diketone must have arisen through combination of two radicals formed by rearrangement :



Condensation also occurs with lævulic acid; the products probably consist mainly of the lactone (III).



EXPERIMENTAL.

(M. p.s are uncorr. Elementary analyses are by Drs. Weiler and Strauss. Identities of known compounds were confirmed by mixed m. p. determinations.)

Methylcyclopentyl and Methylcyclohexyl 1-Hydroperoxides.—These were isolated from the products of oxidation of the corresponding *cycloalkanes* (see Part III).

Reduction.—Methylcyclopentyl hydroperoxide (2.5 g.) and sodium sulphite (6 g.) in water (25 c.c.) were heated on the water-bath and stirred for 1½ hours. On working up of the product in the normal way, a viscous syrup (1.6 g.) was obtained, having b. p. *ca.* 135° and m. p. 35–36°, undepressed on admixture with 1-methylcyclopentanol prepared from methylmagnesium iodide and cyclopentanone.

Thermal Decomposition.—(a) Methylcyclopentyl hydroperoxide (15 g.) was heated under reflux until the peroxide had decomposed (10 hours; after 6 hours the peroxide content was *ca.* 5%). The liquid was then distilled to give fractions (i) (1.5 g.) b. p. 90–120°, (ii) (8.3 g.) b. p. 120–130°, (iii) (1.4 g.) b. p. 130–162°, (iv) (0.5 g.) b. p. 110–135°/25 mm., (v) (0.8 g.) b. p. 135–160°/25 mm., and a residue (1.5 g.).

The main product (fraction ii) contained some methyl butyl ketone (2 : 4-dinitrophenylhydrazone, m. p. 109–110°, undepressed on admixture with a synthetic specimen), but consisted mainly of 1-methylcyclopentanol (phenylurethane, m. p. 88–89°) and 6-hydroxyhexan-2-one, which yielded a *phenylurethane*, m. p. 66–67°, much less soluble in light petroleum (Found : C, 65.9, 66.9; H, 7.4, 7.5; N, 6.4, 6.0. C₁₃H₁₇O₃N requires C, 66.4; H, 7.2; N, 6.0%). Treatment of the second phenylurethane

with 2 : 4-dinitrophenylhydrazine hydrochloride yielded a 2 : 4-dinitrophenylhydrazone, m. p. 120—121.5° (from methanol).

For comparison 6-hydroxyhexan-2-one was synthesised by Lipp's method (*Ber.*, 1885, **18**, 3275; *Annalen*, 1896, **289**, 182 : cf. Colman and Perkin, *J.*, 1889, **55**, 354); it had b. p. 150—154°. It yielded the expected phenylurethane, m. p. 66—67.5°, identical with that recorded above, and this gave a 2 : 4-dinitrophenylhydrazone, m. p. 120—121.5° (Found : C, 55.0; H, 5.3; N, 17.0; $C_{19}H_{21}O_4N_4$ requires C, 54.9; H, 5.3; N, 16.9%), also identical with the compound described above. The ketol provided a 2 : 4-dinitrophenylhydrazone, m. p. 96—97° (Found : N, 19.35; $C_{12}H_{16}O_5N_4$ requires N, 19.6%).

Fraction (iii) yielded two 2 : 4-dinitrophenylhydrazones in small quantity only : (a) m. p. ca. 230°, probably the derivative of a dicarbonyl compound, and (b) m. p. 141—144°, shown by its ultra-violet absorption spectrum to be an $\alpha\beta$ -unsaturated carbonyl derivative, probably produced by oxidation of 1-methylcyclopentene, itself obtained by dehydration of the tertiary alcohol. This fraction also contained some acid.

Fraction (v) afforded *p*-bromophenacyl 5-ketohexanoate, m. p. 90—91°.

Fraction (i) was mainly ketonic and formed a 2 : 4-dinitrophenylhydrazone, m. p. 115.5—116.5°, *i.e.*, higher than that for the corresponding derivative of methyl butyl ketone, but was not depressed on admixture. However, on analysis it appeared to be a derivative of this ketone (Found : C, 51.1; H, 5.5; N, 20.4. Calc. for $C_{12}H_{16}O_4N_4$: C, 51.4; H, 5.7; N, 20.0%). The 2 : 4-dinitrophenylhydrazones of methyl butyl ketone and methyl ethyl ketone do not depress the m. p. of one another.

(b) Methylcyclohexyl hydroperoxide (9.5 g.) was heated at *ca.* 140° for 3 hours, thereby completely decomposing; after 1½ hours only about 1% remained unchanged. Distillation provided fractions, b. p. 100—125° (0.8 g.) and 125—140° (5.5 g.), and a residue (1.5 g.). Both fractions appeared to be mixtures of ketones and alcohols (examination with hydroxylamine hydrochloride and methylmagnesium iodide). Both yielded a 2 : 4-dinitrophenylhydrazone, which after repeated recrystallisation melted at 85—87°, not depressed on admixture with methyl *n*-amyl ketone 2 : 4-dinitrophenylhydrazone. The semicarbazone had m. p. 120—121°, also unaltered on admixture with methyl *n*-amyl ketone semicarbazone. No phenylurethane could be isolated, but synthetic 1-methylcyclohexanol also gave no phenylurethane: the alcohol from the thermal decomposition, however, had an infra-red spectrum similar to that of the synthetic material.

Mineral Acid.—(a) Methylcyclopentyl hydroperoxide (15 g.) and sulphuric acid (10%; 50 c.c.) were heated at 90—100° for 2 hours. The product was extracted with ether and worked up in the normal way. Distillation gave fractions (i) (0.5 g.) b. p. 60—90°, (ii) (1.5 g.) b. p. 90—128°, (iii) (1.8 g.) b. p. 128—135°, (iv) (1.4 g.) b. p. 135—150°, (v) (1.2 g.) b. p. 120—160°/16 mm., (vi) (1.0 g.) b. p. 160—200°/16 mm., and a residue (2.5 g.). Fraction (i) consisted mainly of 1-methylcyclopentene (absorption of bromine in carbon tetrachloride). Fraction (ii) yielded methyl butyl ketone 2 : 4-dinitrophenylhydrazone, m. p. 112—113°. Fraction (iii) contained mainly methyl butyl ketone (2 : 4-dinitrophenylhydrazone) and 6-hydroxyhexan-2-one (phenylurethane, m. p. 67—68°). Fractions (iv) and (v) also contained mainly these two products. Fraction (vi) yielded a small quantity of an unidentified 2 : 4-dinitrophenylhydrazone, m. p. 160—162°. The aqueous layer, after neutralisation, was evaporated to dryness and re-extracted with ether. This gave a further quantity (*ca.* 1 g.) of 6-hydroxyhexan-2-one.

(b) Methylcyclohexyl hydroperoxide (10 g.) and sulphuric acid (20%; 25 c.c.) were heated together on the water-bath, until the peroxide had decomposed (14 hours). Ether-extraction yielded only 5 g. of material, mainly methyl *n*-amyl ketone (2 : 4-dinitrophenylhydrazone, m. p. 91—92°; semicarbazone, m. p. 120—121°). The minor products were not further studied.

Sodium Hydroxide.—(a) To sodium hydroxide (12 g.) in water (50 c.c.) methylcyclopentyl hydroperoxide (15 g.) was added slowly with shaking. The solid sodium salt of the hydroperoxide was first formed, but on slight warming an exothermic reaction ensued resulting in the formation of two layers. The mixture was warmed for a further 1½ hours. Ether-extraction yielded the neutral product (A); the aqueous layer on acidification and re-extraction provided acid material (B). On distillation (A) provided fractions (i) (5.8 g.), b. p. 135—140°, (ii) (2.4 g.) b. p. 140—143°, and (iii) (0.4 g.) b. p. 143—160° (residue, 0.7 g.). Fractions (i) and (ii) contained mainly 1-methylcyclopentanol (phenylurethane, m. p. and mixed m. p. 88—89°) with 15—20% of methyl butyl ketone (2 : 4-dinitrophenylhydrazone, m. p. 108—109°; semicarbazone, m. p. 119—121°). The acids (B) (*ca.* 1 g.) included pyruvic acid (*p*-bromophenacyl ester, m. p. and mixed m. p. 114—115°).

(b) Sodium hydroxide (3.1 g.), water (30 c.c.), and methylcyclohexyl hydroperoxide (10 g.) were heated at 110—120°, 10 hours being necessary for complete destruction of the peroxide. As in (a) a neutral (A) and an acid product (B) were produced. Product (A) distilled entirely at 145—155° (6.1 g.) and analysis showed it to contain ketone *ca.* 15% and alcohol *ca.* 85%. It yielded methyl *n*-amyl ketone 2 : 4-dinitrophenylhydrazone, m. p. 91—92°. The alcohol was presumably 1-methylcyclohexanol. The acids (B) (1.2 g.) provided a small quantity of an unidentified *p*-bromophenacyl ester, m. p. 103—104° (from methanol).

Sodium Carbonate.—Methylcyclopentyl hydroperoxide (9.5 g.) and sodium carbonate (8.7 g.) in water (30 c.c.) were heated on the water-bath for *ca.* 16 hours. As peroxide was then still present, a further quantity of carbonate (8.7 g.) was added and the mixture heated under reflux for a further 8 hours. Although traces of peroxide still remained, the product was worked up as above. The products consisted of a mixture of methyl butyl ketone (2 : 4-dinitrophenylhydrazone) and 6-hydroxyhexan-2-one (phenylurethane).

Butyraldehyde.—Methylcyclopentyl hydroperoxide (12 g.), mixed with *n*-butyraldehyde (10 g.), became warm. After the mixture had been heated on the water-bath for 2 hours, the peroxide content had decreased by 35%. Titration indicated the presence of butyric acid (2.9 g.). After removal of the

unchanged hydroperoxide, aldehyde, and most of the butyric acid by distillation under reduced pressure, increase of the bath-temp. caused rapid decomposition of the residue. This was probably due to the initial production of a hydroxy-peroxide followed by its decomposition in the presence of butyric acid at 120°.

Acetone.—Acetone (30 g.), concentrated hydrochloric acid (15 c.c.), and methylcyclopentyl hydroperoxide (20 g.) were shaken at *ca.* 0° for $\frac{1}{2}$ hour and poured into water. The product was extracted with light petroleum, and the extract dried, evaporated, and distilled. The distillate (15.5 g.) was uniform pure 2 : 2-*di*-(1-methylcyclopentylperoxido)propane, b. p. 82–87°/0.15 mm., n_D^{20} 1.4565 (Found : C, 66.3; H, 10.5%; peroxide equiv., 135. $C_{15}H_{28}O_4$ requires C, 66.17; H, 10.3%; peroxide equiv., 136).

The product (18 g.) was slowly dropped through a heated tube (*ca.* 200°) into a cooled receiver. Part of the condensate was distilled to give fractions: (i) (trace) b. p. 34–55°; (ii) (1.6 g.) b. p. 55–110°; (iii) (1.5 g.) b. p. 42–73°/15 mm.; (iv) (2.0 g.) b. p. 73–110/15 mm.; (v) (0.5 g.) b. p. 110–140°/15 mm.; residue (1.0 g.). The compositions of these were: (i) mainly ether, with a little formaldehyde (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 164°; (ii) methyl butyl ketone (2 : 4-dinitrophenylhydrazone), contaminated by another carbonyl compound; (iii) mainly carbonyl compounds (not resolved); fractions (iv) and (v) crystallised when kept; after recrystallisation from light petroleum the solid dodecane-2 : 11-dione had m. p. 67.5–68.5° (see Part V).

Lævulic Acid.—(a) Methylcyclopentyl hydroperoxide (30 g.), lævulic acid (30 g.), and concentrated hydrochloric acid (15 g.) were shaken at 0° for $\frac{3}{4}$ hour, then poured into water. The lower organic layer was extracted with light petroleum, the extract was washed with water and dried, and the lower-boiling materials removed at the water-pump. The residue was distilled, to give fractions: (i) (1.5 g.) b. p. 30–52° (mainly 45–50°)/0.2 mm.; (ii) (3.5 g.) b. p. 52–70°/0.15 mm.; (iii) (4.2 g.) b. p. 70–82°/0.15 mm.; (iv) (5.7 g.) b. p. 82–83°/0.08 mm.; and a residue (1.2 g.). Fractions (i) and (ii) were mainly unchanged hydroperoxide. Fractions (iii) and (iv) gave the following analytical figures :

	Acid equiv.	Ester equiv.	Peroxide equiv.	% Active hydrogen.	Mol. wt. (cryoscopic).
Fraction (iii)	7305	608	198	0.11	114 (?)
Fraction (iv)	2035	230	450 *	0.20	223
$C_{16}H_{18}O_4$ (III)	—	214	214	nil	214

* Variable, depending on the time of heating with KI-AcOH, owing to slow liberation of iodine.

The variation of the ester equivs. and peroxide equivs. between fractions (iii) and (iv) show the presence of two different compounds, but their constitutions appear uncertain from the above data. The figures, however, appear definitely to exclude the acid derived from (III), which would require an acid equiv. of 232 and an active hydrogen content of 0.86%.

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