540. *Reactions of Organic Peroxides. Part III. Oxidation of Methyl*cyclo*pentane and Methyl*cyclo*hexane.*

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Liquid-phase oxidation of methyl*cyclo*pentane and methyl*cyclo*hexane at 100—130° under pressure yields some hydroperoxides, but continuation of the oxidation beyond a limited stage causes rapid decomposition of the peroxides and formation of alcohols, ketones, acids, and lactones. Such of these products as have been identified may arise from radicals produced from the hydroperoxides.

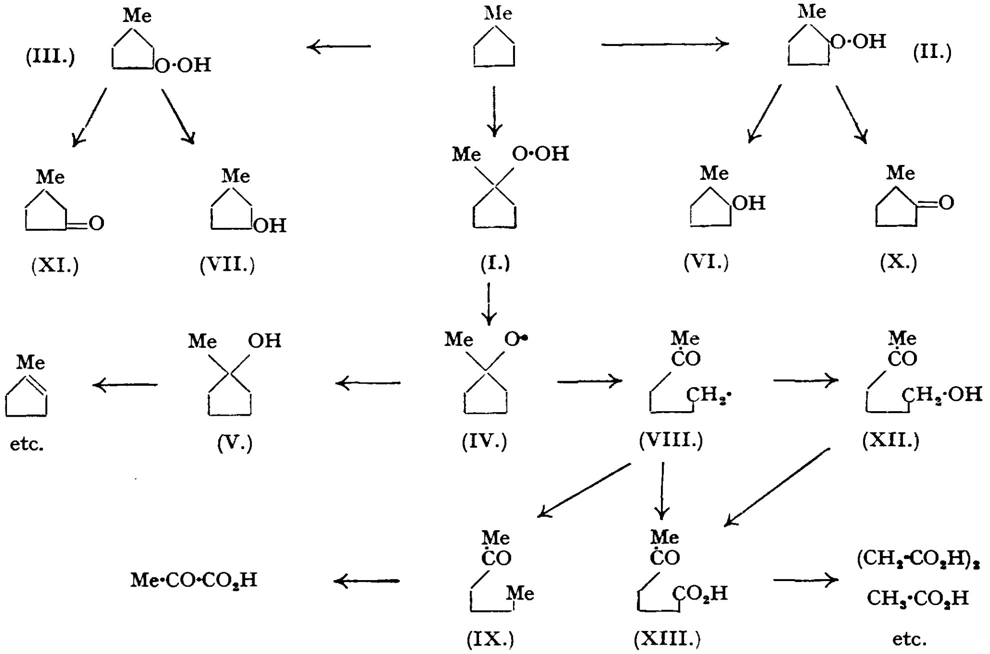
Chavanne and his co-workers (*inter al., Bull. Soc. chim. Belg.*, 1927, **36**, 206; 1930, **39**, 206, 287; 1931, **40**, 611, 626; 1932, **41**, 209; 1933, **42**, 537) found that most of the oxidation products of many alkyl*cyclo*paraffins studied arose from attack at the tertiary carbon atom, followed by ring opening. The compounds thus formed were tertiary alcohols, ketones, keto-acids, and, in smaller amounts, degradation products formed by further oxidation. From dialkyl-substituted hydrocarbons ditertiary alcohols and diketones were similarly produced. Very probably all these products were derived from hydroperoxides first formed, although such compounds were not isolated.

The oxidation of methyl*cyclo*pentane has now been studied; the products formed confirm Chavanne's results and also include the intermediate hydroperoxide. Liquid-phase oxidations were carried out at 100—130° under pressure, with and without catalysts; varying the conditions altered little except relative amounts of the products. A hydroperoxide was first formed, but was later accompanied by increasing quantities of alcohols, ketones, lactones, and acids, until at about 8% peroxide concentration the decomposition of the hydroperoxide proceeded more rapidly than its formation. Many of the compounds isolated are accounted for in the scheme on p. 2799.

On initial oxidation the methyl*cyclo*pentane may give any of the hydroperoxides (I), (II), or (III), although it would be expected that the major product would be (I). This tertiary hydroperoxide would provide 1-methyl*cyclo*pentanol (V) *via* the radical (IV), whilst the corresponding radicals from the 2- and 3-hydroperoxides would yield 2- and 3-methyl*cyclo*pentanol (VI and VII), or 2- and 3-methyl*cyclo*pentanone (X and XI). 1-Methyl*cyclo*pentanol, 3-methyl*cyclo*pentanone, and traces of various unidentified alcohols and ketones have been found amongst the products.

Many of the oxidation products can best be accounted for by rearrangement of the radical (IV) to the radical (VIII). This can then either gain hydrogen to yield methyl *n*-butyl ketone (IX), gain a hydroxyl radical to form 6-hydroxyhexan-2-one (XII), or be further oxidised to

5-ketohexanoic acid (XIII). All three compounds have been identified in the products of oxidation. The ketohexanoic acid or methyl butyl ketone might further be oxidised (cf. Robertson and Waters, *J.*, 1948, 1574) to succinic and acetic acids or by gradual degradation yield formic acid, pyruvic acid, etc. Formic, acetic, pyruvic, and succinic acids were all found.



Lactones of unknown structure have also been found; they are probably derived from the C_5 or C_6 hydroxy-acids, and may arise by peroxidation of a ketone [cf. the reaction of perbenzoic acid with cyclic ketones (Friess, *J. Amer. Chem. Soc.*, 1949, **71**, 2571)].

The 1-hydroperoxide was obtained pure by repeated extraction with cold alkali and regeneration from the sodium salt with carbon dioxide.

From similar oxidations of methyl*cyclo*hexane the corresponding 1-hydroperoxide was obtained; the other products were not examined in detail but also appeared to consist of alcohols, ketones, and acids.

The reactions of these hydroperoxides are considered later (Parts IV and V).

EXPERIMENTAL.

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

*Methyl*cyclo*pentane.*—The hydrocarbon used in these oxidation experiments was derived from (*a*) isomerisation of *cyclo*hexane with aluminium chloride (Nenitzescu and Cantuniari, *Ber.*, 1933, **66**, 1097; Glasebrook and Lovell, *J. Amer. Chem. Soc.*, 1939, **61**, 1717), and (*b*) a petroleum fraction (supplied by Anglo-Iranian Oil Co.). In both cases the methyl*cyclo*pentane, when required pure, was passed through a column of silica gel to remove aromatic compounds.

Oxidations.—In preliminary oxidation experiments at 40—50°/1 atm. absorption of oxygen was too slow. Pressure oxidation at a higher temperature were carried out batchwise and continuously in two apparatus :

(*a*) Air was introduced through a sintered-glass disc at the bottom of an electrically-heated Pyrex-glass column (5 ft. long; 1 in. in internal diameter), and the exit vapours were passed through stainless-steel cooling traps. In the continuous runs the hydrocarbon was fed in at the top of the reactor, and the product removed at the base. The temperatures were 100° to 135°, and the pressure from 50 to 75 lbs./sq. in. The peroxide content of the crude product from this apparatus rarely rose above 5—7% w/v, and, if the oxidation proceeded too far, the peroxide content fell and the acid and lactone content rose.

(*b*) The compound was stirred in a stainless-steel reactor (12 in. × 4 in.), at *ca.* 1400 revs./min. The temperature was generally 130° and pressures varied from 75 to 200 lbs./sq. in. Again the peroxide content of the crude product under the best conditions reached 7—8%, but decomposition products were also present.

Addition of sodium carbonate or metal-salt catalysts during the oxidation led to more rapid decomposition of the peroxide; the presence of magnesium oxide gave rise to the best conversion into peroxide (*ca.* 8% w/v) (cf. U.S.P. 2,430,864, 2,430,865).

1-*Methyl*cyclo*pentyl Hydroperoxide.*—The hydroperoxide was isolated from the crude oxidate in two ways: (*a*) by direct extraction with 50% sodium hydroxide solution, whereupon the sodium salt crystallised and was removed by filtration, and (*b*) by concentration of the peroxide in a climbing-film evaporator, followed by conversion into the sodium salt.

The free acids were first removed by shaking the crude product with saturated aqueous potassium carbonate, and the organic layer was then shaken with 50% sodium hydroxide solution, with cooling if necessary. The sodium salt was filtered off, washed with light petroleum to remove adsorbed organic products, and suspended in water, and carbon dioxide passed into the ice-cooled suspension. Lack of cooling during these operations generally led to some decomposition of the hydroperoxide. The free hydroperoxide was extracted with benzene, the benzene solution dried, and the solvent removed under reduced pressure. The hydroperoxide was distilled under reduced pressure and was then *ca.* 95% pure. Repetition of the above process gave a purer product, although a loss of 20—40% of the hydroperoxide resulted from its incomplete removal as sodium salt. The purified hydroperoxide had b. p. 26—28°/0·25 mm., 73·5°/19 mm., and n_D^{20} 1·4526 (Found: C, 62·7, 62·9; H, 10·5, 10·35. Calc. for $C_6H_{12}O_2$: C, 61·1; H, 10·3%).

During the sodium hydroxide extraction (*a*) there was a loss of peroxidic material through decomposition; in method (*b*) the residues contained peroxides which similarly decomposed on alkali treatment. Attempts to purify this alkali-unstable peroxide had little success owing to its thermal instability. It was probably a condensation product of the hydroperoxide with a ketone or keto-acid.

Other Oxidation Products.—(*a*) Methyl*cyclo*pentane (450 g.) was oxidised in the glass column at 120° until 45 l. of oxygen (as air) had been absorbed, cobalt stearate being used as catalyst, so that no appreciable amount of peroxide remained at the end of the oxidation. The product consisted of (i) an upper organic and (ii) a lower aqueous layer.

(i) The upper layer was stripped of the bulk of the unchanged hydrocarbon and then distilled. Fraction 1, b. p. 78—82° (11 g.), consisted mainly of unchanged hydrocarbon. From fraction 2, b. p. 82—128° (1·5 g.), methyl butyl ketone 2 : 4-dinitrophenylhydrazone, m. p. 115—117° after recrystallisation, was isolated. From fraction 3, b. p. 128—140° (4·7 g.), the same 2 : 4-dinitrophenylhydrazone, m. p. 110—113°, and 1-methyl*cyclo*pentyl phenylurethane, m. p. 89—90°, were obtained. Fraction 4, b. p. 140—148° (7 g.), yielded a 2 : 4-dinitrophenylhydrazone, which after several recrystallisations had m. p. 124—125·5°, but was still not pure; admixture with the corresponding derivative of 3-methyl*cyclo*pentanone raised the m. p. to 134—136°, whilst admixture with the derivatives of methyl butyl ketone and 2-methyl*cyclo*pentanone depressed the m. p. This fraction was probably a mixture including 3-methyl*cyclo*pentanone. Fraction 5, b. p. 60—100°/18 mm. (2·8 g.), was also a mixture, but repeated recrystallisation of the 2 : 4-dinitrophenylhydrazone yielded the slightly impure derivative, m. p. 135—138°, of 3-methyl*cyclo*pentanone (Found: C, 51·2; H, 5·0; N, 19·7. Calc. for $C_{12}H_{14}O_4N_4$: C, 51·8; H, 5·0; N, 20·15%). Fractions 6 (2·4 g.), 7 (3·3 g.), and 8 (b. p. 100—220°/16 mm.; 3·3 g.), on their analytical data, evidently contained high proportions of esters; no pure, clearly defined carbonyl derivatives could be obtained, but, after hydrolysis, the acid portion from fraction 7 (b. p. 150—170°/16 mm.) yielded 5-ketohexanoic acid 2 : 4-dinitrophenylhydrazone, m. p. 135°, and semicarbazone, m. p. 173—174°. Hydrolysis of fraction 8 provided acid material insoluble in benzene, which after recrystallisation from hot water was shown by its m. p. and equivalent to be succinic acid. The last three fractions therefore contained mixtures of ketones, acids, and esters (or lactones).

(ii) The aqueous layer was extremely acid, and was extracted with ether, to remove part of the product. The ethereal extract (ii*a*) was fractionated, and afforded derivatives of methyl butyl ketone and 3-methyl*cyclo*pentanone. In addition, a fraction, b. p. 98—160°/18 mm. (1·3 g.), yielded probably impure dodecane-2 : 11-dione 2 : 4-dinitrophenylhydrazone, m. p. 159—161° (see Part V). Fractions, b. p. 134—150° (9·1 g.), provided 1-methyl*cyclo*pentyl phenylurethane, m. p. 88—89°, and the fraction, b. p. 142—150° (4·3 g.), further yielded a 5-ketohexyl phenylurethane, m. p. 66—67°, which was much more insoluble in light petroleum (see Part IV).

The remaining aqueous solution (ii*b*) was hydrolysed and the aqueous solution evaporated to dryness under reduced pressure. The sodium salts were suspended in ether and treated with hydrogen chloride, the inorganic material was filtered off, and the ethereal solution evaporated and distilled. Fraction 1, b. p. 108—118°, provided *p*-bromophenacyl formate, m. p. 139—141°, whilst both fractions 1 and 2 (b. p. 118—130°) (together 3·6 g.) yielded *p*-bromophenacyl acetate, m. p. 83—84°. Fraction 3, b. p. 130—140° (0·57 g.), gave *p*-bromophenacyl pyruvate, m. p. 114—115°. No derivative was obtained from fraction 4, b. p. 140—198°; this and later fractions [especially 5 (b. p. 198—225°) (2·37 g.) and 6 (b. p. 225—240°/760 mm.) (0·54 g.)] probably contained lactones, as indicated by their low ester equivalents (170—289). Fraction 5 gave slightly impure *p*-bromophenacyl succinate, m. p. 205—208°. Fraction 6 afforded an unidentified *p*-bromophenacyl ester, m. p. 140—142°. Fraction 7, b. p. 152—194°/50 mm. (1·07 g.), on cooling gave crystals of succinic acid, m. p. 181—182°, and also *p*-bromophenacyl 5-ketohexanoate, m. p. 93—94°.

(*b*) The aqueous layers from six more carefully controlled oxidation experiments (without added catalyst) were combined. After removal of the water the product was distilled. The lower-boiling fractions (up to 170°) (33·2 g.) contained ketones similar to those recorded above, 1-methyl*cyclo*pentanol, and (mainly acetic) acid. Hydrolysis of fractions, b. p. 79—105°/16 mm. (16·0 g.), yielded mainly a product, b. p. 190—200°; titration indicated that this consisted mainly of lactones and it was not further examined. Hydrolysis of a fraction, b. p. 105—130°/16 mm. (5·6 g.), yielded 6-hydroxyhexan-2-one, a lactone, and a little succinic acid (*p*-bromophenacyl ester). Hydrolysis of fractions, b. p. 112—

180°/5 mm. (24·8 g.), gave the ketol and 5-ketohexanoic acid. The following derivatives of this acid were obtained :

		Found, %.				Calc., %.		
	M. p.	C.	H.	Br.	Formula.	C.	H.	Br.
$Me{\cdot}CO{\cdot}[CH_2]_3{\cdot}CO_2H,H_2O$ ...	35—37°	48·7	7·95	—	$C_6H_{12}O_4$	48·65	8·1	—
p-Bromophenacyl ester ...	92—92·5	51·2	4·4	25·0	$C_{14}H_{15}O_4Br$	51·4	4·6	24·5
Semicarbazone	171·5—172·5	44·7	7·2	—	$C_7H_{13}O_3N_3$	44·9	7·0	—
2 : 4-Dinitrophenylhydrazone	134—136	46·7	4·4	—	$C_{12}H_{14}O_6N_4$	46·45	4·5	—

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