# 297. 1-*Hydroxy*cyclo*hexyl* 1-*Hydroperoxide: its Thermal Decomposition and its Reaction with Acyl Chlorides.*

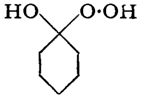
By W. Cooper.

1-Hydroxy*cyclo*hexyl 1-hydroperoxide decomposes when heated, giving free radicals, and the products formed are explicable by the mechanism proposed by George and Walsh (*Trans. Faraday Soc.*, 1946, **42**, 94) for the decomposition of *tert.*-alkyl peroxides. On reaction with acyl chlorides it forms per-esters which are active polymerisation catalysts.

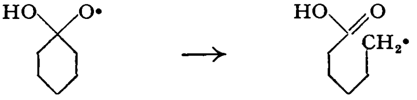
*cyclo*Hexanone reacts with hydrogen peroxide to give 1-hydroxy*cyclo*hexyl 1-hydroperoxide (I), which readily self-condenses to give the peroxides, bis-1-hydroxy*cyclo*hexyl peroxide, 1-hydroperoxy*cyclo*hexyl 1-hydroxy*cyclo*hexyl peroxide, and the dihydroperoxy-peroxide (Milas, Harris, and Panagiotakos, *J. Amer. Chem. Soc.*, 1939, **61**, 2430; Criegee, Schnorrenberg, and Becke, *Annalen*, 1949, **565**, 7).

This paper deals with the reactions of (I), and, though the participation of the peroxides in the decomposition cannot be excluded, their presence does not alter the argument concerning the mechanism of the reaction.

The peroxides are formed in the oxidation of *cyclo*hexanone by Caro's acid or perbenzoic acid, the peroxide link undergoing heterolysis (Friess, *J. Amer. Chem. Soc.*, 1949, **71**, 2571). Thermal decomposition, however, favours homolysis, and, if the mechanism proposed by George and Walsh (*loc. cit.*) holds for these peroxides, the free radicals (II) and (III) would be formed. The usual type of radical-deactivation reactions would then give hexanoic acid, dodecane-1 : 12-dioic acid, and 6-hydroxyhexanoic acid.*



(I.)



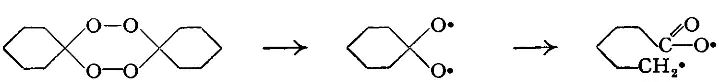
(II.) (III.)

The products of the thermal decomposition of (I) at 120—160° included the first two of these acids, together with carbon dioxide, water, *cyclo*hexanone, di*cyclo*hexylidene diperoxide (IV), and adipic acid. This last may have resulted from the oxidation of 6-hydroxyhexanoic acid.

Disproportionation of (III) by the reaction

$$2\,(\text{III}) \longrightarrow \text{CH}_2\text{:CH}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H} + \text{CH}_3\cdot[\text{CH}_2]_4\cdot\text{CO}_2\text{H}$$

is unlikely since unsaturated acids were not found, nor was there any appreciable amount of glutaric acid present. There would be little gain in energy to favour such a reaction. Hawkins (*J.*, 1950, 2804) finds that dimerisation of 5-ketohexyl radicals from 1-methyl*cyclo*pentane hydroperoxide is a major reaction.



(IV.) (V.)

The diperoxide (IV) clearly results from the dehydration of two molecules of the hydroperoxide, since it may be obtained by treating (I) in ether solution with phosphoric oxide or in alcohol with 70% sulphuric acid. It is very stable, and does not liberate iodine from potassium iodide or catalyse vinyl polymerisations. It explodes mildly at 190—200°, giving *cyclo*hexanone and acidic compounds; these were not examined in detail, but, in addition to simple carboxylic acids (probably including hexanoic acid), an insoluble, high-melting polymer was formed. This dissolved in hot alkalis, and was probably derived from the radical (V). In the decomposition of (I), the large amount of *cyclo*hexanone resulted from elimination of hydrogen peroxide, from condensation reactions, or from (II).

The hydroperoxide (I) is a useful polymerisation catalyst, but experiments indicating that

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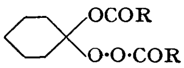
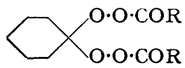
* Geneva nomenclature, $CO_2H$ = 1.

not all of it was consumed in starting polymer chains led to experiments to prepare more efficient acyl derivatives. The hydroperoxide could not be made to react with acyl chlorides in the presence of aqueous alkali, but with an excess of pyridine reaction occurred to form a new series of organic peroxides. Acetyl, benzoyl, *o*-chlorobenzoyl, and *p*-bromobenzoyl derivatives were obtained pure, and also *m*-nitrobenzoyl and phenylacetyl derivatives less pure. The properties of these compounds did not support structure (VI) and, although absolute proof of their structure is lacking, the following evidence suggesting (VII) was obtained : (*a*) Treatment with alcoholic potassium hydroxide gave exclusively the carboxylic acid, *cyclo*hexanone, and

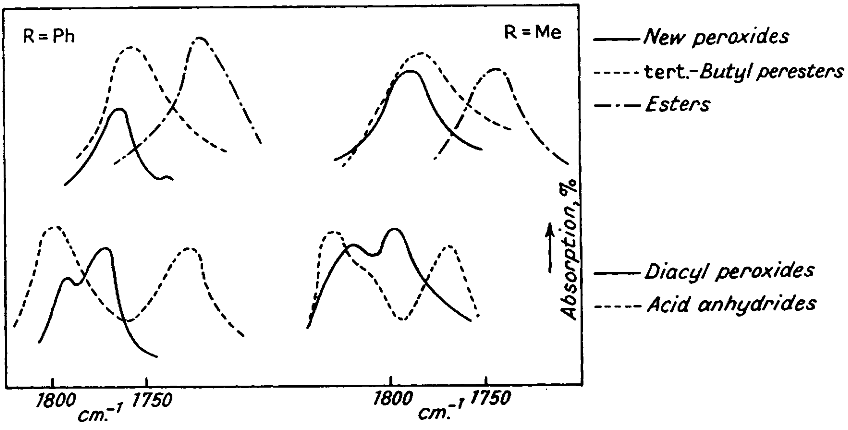
(VI.)





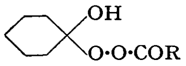
(VII.)

oxygen. (*b*) The benzoyl and *p*-bromobenzoyl derivatives gave 71% and 77% of the corresponding acids. This evidence and the molecular weights show that they contain two acyl and one *cyclo*hexyl group, and also that they are not condensed structures containing more than one *cyclo*hexyl grouping. (*c*) They are per-esters, and their infra-red spectra show only one carbonyl absorption at the per-ester frequency; (VI) would give one ester and one per-ester frequency, whereas in (VII) negligible mechanical interaction between the two carbonyl groups would give the single absorption (figure). (The infra-red examination formed part of a study on the relation between carbonyl frequency and structure, by Davison, which is now in the press.) The *o*-chlorobenzoyl derivative decomposed faster than the benzoyl derivative, as shown by the rate of polymerisation of styrene, indicating the proximity of the halogen atom to the peroxide link (the relation between peroxide structure and decomposition rate is dealt with in a forthcoming paper). (*d*) The liberation of iodine from acidified potassium iodide, though incomplete, was greater than would be expected for (VI). (*e*) Carbon and hydrogen values were unreliable because of the very explosive character of peroxides, but were in better agreement with structure (VII) than with (VI).



*Infra-red carbonyl absorption of compounds containing the* RCO·O– *grouping.*

It is difficult to suggest a plausible mechanism for the formation of these peroxides, except by assuming that one molecule of the hydroperoxide is used in the conversion of the acyl chloride into the corresponding peracid, which then reacts with the half acylated compound :



$$+ \text{RCO·O·OH} \longrightarrow \text{(VII)} + \text{H}_2\text{O}$$

The evidence for this suggestion is scanty, but two significant facts are that (*a*) three moles of acyl chloride per mole of hydroperoxide were needed to give a reasonable yield of the derivative, and (*b*) the final mixture contained considerable quantities of free carboxylic acid, which showed that water was eliminated at some stage in the reaction. A similar difficulty is presented in the explanation of the mechanism of formation of the dihydroperoxy-peroxide, as this compound cannot be represented by a simple condensation of (I) or its constituents.

The acyl peroxides are efficient catalysts for the polymerisation of styrene. The following table gives results obtained with this monomer at 70°, together with values for the parent hydroperoxide and dibenzoyl peroxide.

| Catalyst. | Concentration, g./l. | mole/l.[a] | Polymn. rate, mole/l./sec. × $10^4$ | [$\eta$].[b] |
|---|---|---|---|---|
| Acetyl derivative | 3·25 | 0·028 | 1·91 | 0·52 |
| Benzoyl derivative | 4·95 | 0·028 | 1·99 | 0·56 |
| *o*-Chlorobenzoyl derivative | 5·95 | 0·028 | 2·35 | 0·49 |
| Dibenzoyl peroxide | 6·80 | 0·028 | 1·80 | 0·47 |
| | 3·40 | 0·014 | 1·27 | 0·69 |
| 1-Hydroxy*cyclo*hexyl hydroperoxide | 1·85 | 0·014 | 1·50 | 0·50 |

[a] Calculated on the active-oxygen content of the peroxide. [b] Intrinsic viscosity of the polymer in benzene.

## EXPERIMENTAL.

*1-Hydroxy*cyclo*hexyl 1-Hydroperoxide.*—*cyclo*Hexanone was mixed with an equal volume of 30% hydrogen peroxide. Next morning the crystals were removed and recrystallised from alcohol and then light petroleum (b. p. 60—80°). The peroxide had m. p. 79° [Found: equiv. (iodometric), 131; *M* (cryoscopic in benzene), 222. Calc. for $C_6H_{12}O_3$: equiv., 132; *M*, 132]. The molecular weight value was high probably because of association by hydrogen bonding.

*Thermal Decomposition of 1-Hydroxy*cyclo*hexyl 1-Hydroperoxide.*—The relative proportions of products isolated varied with temperature in the range 110—160°, but the same compounds were formed in all cases. The hydroperoxide was dropped in small amounts into a flask at 130—140°. A vigorous initial reaction was followed by a smooth decomposition with the evolution of some carbon dioxide. The residue (47·5 g. from 50 g. of hydroperoxide) gave a negative test for peroxide. To it was added N-sodium hydroxide (250 ml.), and the insoluble portion was extracted with ether. The extract (14 g.) was principally *cyclo*hexanone (b. p. 155°; 2 : 4-dinitrophenylhydrazone, m. p. 159°), but in some cases crystalline di*cyclo*hexylidene diperoxide (IV), m. p. 129°, was isolated [Found: C, 63·0; H, 8·75%; *M* (cryoscopic in benzene), 220. Calc. for $C_{12}H_{20}O_4$: C, 63·4; H, 8·8%; *M*, 228]. The aqueous layer gave liquid acids (19 g.) which were separated into three fractions:

(1) 45%, b. p. 95—105°/20 mm. This was mainly hexanoic acid [Found: equiv. (silver salt), 113. Calc. for $C_6H_{12}O_2$: equiv., 116]; anilide, m. p. 95°; amide, m. p. 99° (the melting points were not depressed on admixture of these specimens with authentic samples).

(2) 20%, b. p. 180—220°/20 mm. This gave adipic acid, m. p. 149—150° [Found: equiv. (by titration), 73. Calc. for $C_6H_{10}O_4$: equiv., 73].

(3) 15%, b. p. 220—280°/20 mm. This yellow oil, which deposited crystals on cooling, was extracted several times with large amounts of hot water. When these extracts had cooled there were obtained flat lustrous crystals, which were recrystallised from light petroleum (b. p. 60—80°), ether–light petroleum, and hot water, giving dodecane-1 : 12-dioic acid, m. p. 127°: diamide, m. p. 185°; dianilide, m. p. 169° [Found: C, 62·6; H, 9·9%; equiv. (silver salt and by titration), 113. Calc. for $C_{12}H_{22}O_4$: C, 62·6; H, 9·6%; equiv., 115]. The acid did not depress the m. p. of the synthetic acid prepared from sebacic acid, and showed the same infra-red skeletal absorptions in the 700—1300-cm.$^{-1}$ region. The more water-soluble acids from the decomposition products were isolated and purified through their ethyl esters. Adipic acid was identified, and there was a trace of another acid, very soluble in water, which was probably glutaric acid.

*Decomposition of Di*cyclo*hexylidene Diperoxide.*—This compound (1 g.) was decomposed in small portions at 190—200°. The residue contained neutral products including *cyclo*hexanone, a brown solid which was insoluble in cold dilute alkali or organic solvents, and decomposed before melting, and liquid acids probably containing hexanoic acid. The brown solid dissolved in hot alkalis and on acidification of the alkaline solution regenerated a semi-solid acid, soluble in alcohol.

*Reaction of 1-Hydroxy*cyclo*hexyl Hydroperoxide with Acyl Chlorides.*—The peroxide (1 mole) was dissolved in pyridine (5 moles) and the acyl chloride (3 moles) added slowly, the temperature being kept below 10°. After one hour the mixture was poured into water; acetyl and benzoyl chlorides gave oily products which deposited crystals on cooling, whilst with *m*-nitro- and *p*-bromo-benzoyl chlorides the peroxides were extracted with benzene from the solid precipitate of peroxide and carboxylic acid. The peroxides were recrystallised from benzene–alcohol, precautions being taken because of the explosive nature of the compounds—particularly the acetyl derivative. Boiling the peroxides in alcoholic solution caused decomposition with the formation of the carboxylic acid. The analysis of these compounds was difficult, because of their explosiveness, ease of decomposition in solution, and their incomplete reaction with potassium iodide. The following acyl derivatives were obtained: *benzoyl*, m. p. 97 [Found: C, 67·5; H, 5·9%; *M* (cryoscopic in benzene), 342, 350; (in dioxan), 357; equiv. (iodometric), 186—211. $C_{20}H_{20}O_6$ requires C, 67·5; H, 5·6%; *M*, 356; equiv., 178]; p-*bromobenzoyl*, m. p. 104° [Found: Br, 31·6%; *M* (in benzene), 471; equiv. (iodometric), 260—300. $C_{20}H_{18}O_6Br_2$ requires Br, 31·2%; *M*, 514; equiv., 257]; o-*chlorobenzoyl*, m. p. 70° [Found: *M* (benzene), 378; equiv., 205. $C_{20}H_{18}O_6Cl_2$ requires *M*, 425; equiv., 212·5]; *m*-nitrobenzoyl, m. p. 116°, not obtained pure; *acetyl*, m. p. 73° [Found: *M* (benzene), 210, 230; equiv., 129—131. $C_{10}H_{16}O_6$ requires *M*, 232; equiv., 116].

*Formation of a Carboxylic Acid during the Preparation of Acyl Derivatives.*—The hydroperoxide (1·5 g.) in pyridine was treated with *p*-bromobenzoyl chloride (6 g.), and the mixture poured into light petroleum and filtered. The solid was washed with benzene, and the pyridine hydrochloride removed; there was left *p*-bromobenzoic acid (m. p. 220°) (1·9 g.). The petroleum–benzene extracts were shaken with dilute ammonia solution, giving more (0·3 g.) of the carboxylic acid. The upper layer after removal of solvents gave crude peroxide (3·3 g.).

*Reaction with Alcoholic Alkalis.*—The peroxides dissolved readily in benzene and the addition of alcoholic potassium hydroxide to the solution caused an immediate liberation of oxygen. The residue after the solvents had been removed by distillation was acidified and the carboxylic acid extracted quantitatively. The distillate contained *cyclo*hexanone (2 : 4-dinitrophenylhydrazone, m. p. 159—160°).

The experimental details of the polymerisation of styrene, and the examination of the polymers are given in a paper to be published later.

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