206. *The Decomposition of* 1-*Phenyl*cyclo*hexyl Peroxides.*

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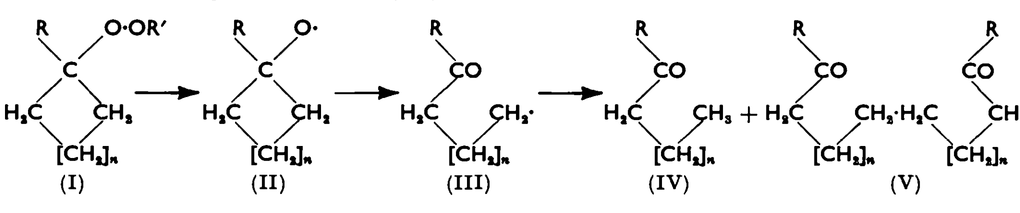
1-Phenyl*cyclo*hexyl hydroperoxide and di-(1-phenyl*cyclo*hexyl) peroxide have been prepared. The thermal decomposition of di-(1-phenyl*cyclo*hexyl) peroxide in chlorobenzene and in pyridine gave *n*-pentyl phenyl ketone, 1 : 10-dibenzoyldecane, and an unidentified ketone, m. p. 104·5°. The thermal decomposition of the hydroperoxide in chlorobenzene gave *n*-pentyl phenyl ketone, but on treatment with aqueous ferrous sulphate it gave 1 : 10-dibenzoyldecane.

Hawkins,[1] in a study of the thermal decomposition of 1-methyl*cyclo*pentyl and 1-methyl*cyclo*hexyl hydroperoxide, obtained products consistent with the formation of the radicals (II and III; R = Me, R′ = H; $n = 2$ and 3 respectively). Hawkins and Young[2] showed that 1-methyl*cyclo*pentyl hydroperoxide reacts with ferrous sulphate to give dodecane-2 : 11-dione (V; R = Me; $n = 2$), which was considered to arise by the dimerisation of the radical (III; R = Me; $n = 2$). Corresponding results were obtained with 1-methyl*cyclo*hexyl hydroperoxide. It was clear, therefore, that oxygen–oxygen fission of the hydroperoxide to give the radical (II) was followed by ring-scission and rearrangement to give the radical (III).



Earlier, Chavanne and his co-workers[3] had found that the autoxidation of substituted *cyclo*pentanes and *cyclo*hexanes, among them 1-phenyl*cyclo*pentane, yielded open-chain oxygenated products of the same type as those obtained by Hawkins. Although it is possible that hydroperoxides were formed initially in these reactions, no direct evidence of their presence was reported.

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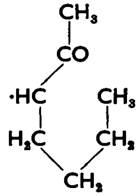
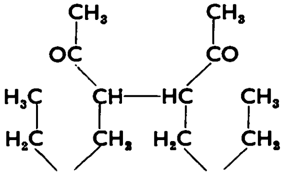
[1] Hawkins, *J.*, 1950, 2801.
[2] Hawkins and Young, *J.*, 1950, 2804.
[3] For references see Hawkins, *Quart. Rev.*, 1950, **4**, 251.

No study of the thermal decomposition of tertiary alicyclic peroxides in which the exocyclic group R is aryl has yet been made. In principle, it is possible for a radical of type (II) to brèak down in two ways : (*a*) by ring scission with the formation of a ketonic radical as above, or (*b*) by elimination of the group R with the formation of a cyclic ketone. In the present communication, an investigation of the decomposition of 1-phenyl*cyclo*hexyl hydroperoxide (I; R = Ph, R′ = H; *n* = 3) and di-(1-phenyl*cyclo*hexyl) peroxide (I; R = Ph, R′ = 1-phenyl*cyclo*hexyl; *n* = 3), in which phenyl radicals may be formed by mechanism (*b*), is reported. Neither di-(1-phenyl*cyclo*hexyl) peroxide nor the hydroperoxide has previously been prepared in a pure state, although the autoxidation of 1-phenyl*cyclo*hexane has been reported[4, 5] to give a product which contained 18% of 1-phenyl*cyclo*hexyl hydroperoxide. Some confusion, however, exists as to whether a pure product can be obtained from this reaction, but in neither case were the properties of the hydroperoxide reported. In the present work, attempts to prepare 1-phenyl*cyclo*hexyl hydroperoxide by the reaction of 1-phenyl*cyclo*hexanol with 30% hydrogen peroxide and sulphuric acid failed. It was, however, obtained in 75% yield from 1-phenyl*cyclo*hexanol by the general method described by Davies, Foster, and White.[6] Di-(1-phenyl*cyclo*hexyl) peroxide was prepared in low yield by condensation of the hydroperoxide with 1-phenyl*cyclo*hexanol in the presence of a catalytic quantity of toluene-*p*-sulphonic acid.[7]

The thermal decomposition of di-(1-phenyl*cyclo*hexyl) peroxide in chlorobenzene and in pyridine yielded *n*-pentyl phenyl ketone (37% and 21% respectively) together with two solid ketones which melted at 97° and 104·5°. The former was identified by comparison with an authentic synthetic specimen as 1 : 10-dibenzoyldecane, but the ketone of m. p. 104·5° was not identified. Milas and Perry[8] isolated 3 : 4-di-*n*-butylhexane-2 : 5-dione (VII) from the decomposition products of *tert.*-butyl-1-methyl*cyclo*hexyl peroxide (I; R = Me, R′ = Bu^t; *n* = 3). This product was considered to arise by rearrangement of the radical (II; R = Me; *n* = 3), produced by the initial homolysis, to give the radical (VI), which then dimerised. The unknown ketone obtained in the present investigation, however, failed to give a pyrrole derivative on treatment with ammonium acetate and glacial acetic acid.[9] This compound is therefore probably not a 1 : 4-diketone analogous to (VII).



(VI)



(VII)

The decomposition of 1-phenyl*cyclo*hexyl hydroperoxide in chlorobenzene gave *n*-pentyl phenyl ketone, but neither of the solid ketones obtained from the experiments with the symmetrical peroxide could be isolated. Treatment of the hydroperoxide with ferrous sulphate by Hawkins and Young's procedure,[2] however, gave 1 : 10-dibenzoyldecane in 22% yield. None of the ketone, m. p. 104·5°, was isolated from this reaction.

In the experiments on the thermal decomposition of di-(1-phenyl*cyclo*hexyl) peroxide and of the hydroperoxide in chlorobenzene and pyridine, no evidence was obtained for the formation of derivatives of diphenyl or phenylpyridine, and it is clear that elimination of a phenyl radical from the 1-phenyl*cyclo*hexyloxy-radical (II; R = Ph; *n* = 3), which is initially produced, does not occur. In addition, *cyclo*hexanone could not be detected in

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[4] Monsanto Ltd., B.P. 681,613.
[5] Rhone-Poulenc Ltd., B.P. 712,264.
[6] Davies, Foster, and White, *J.*, 1953, 1541.
[7] Hercules Powder Co., U.S.P. 2,668,180.
[8] Milas and Perry, *J. Amer. Chem. Soc.*, 1946, **68**, 1938.
[9] Kapf and Paal, *Ber.*, 1888, **21**, 3053.

the products and its absence confirms that cleavage of the bond between the aromatic nucleus and the *cyclo*hexane ring does not take place. This preferential cleavage of the alicyclic ring is clearly due to the considerable loss of the resonance energy arising from the conjugation of the carbonyl group with the aromatic nucleus, which would be involved in the disruption of the radical (II) by mechanism (*b*). It is evident, therefore, that the decomposition of the 1-phenyl*cyclo*hexyl peroxides follows the pattern observed by Hawkins and Young with the methyl analogues. The radical (II; R = Ph; $n = 3$) undergoes ring scission to give the radical (III; R = Ph; $n = 3$). This radical then either disproportionates or abstracts hydrogen from the peroxide or a subsequent decomposition product with the formation of the main product, *n*-pentyl phenyl ketone (IV; R = Ph; $n = 3$). Dimerisation of the same radical yields 1 : 10-dibenzoyldecane. Disproportionation of the radical (III; R = Ph; $n = 3$) would lead to the formation of unsaturated products which, on subsequent attack by other radicals, would give polymers. This may explain the formation of the high-boiling intractable residues (60—70%) that are encountered in these reactions.

EXPERIMENTAL

All solids were crystallised to constant m. p. The light petroleum used had b. p. 40—60°.

1-*Phenyl*cyclo*hexyl Hydroperoxide*.—A suspension of 1-phenyl*cyclo*hexanol [10] (7·3 g.) in ether (10 ml.) was added to a solution of concentrated sulphuric acid (0·04 ml.) in 86% hydrogen peroxide (10 ml.). The mixture was stirred for 6 hr. at room temperature, and water (50 ml.) was then added and the organic layer separated. The aqueous layer was extracted with ether (2 × 25 ml.), and the combined ethereal solutions were extracted with saturated aqueous sodium hydrogen carbonate (2 × 25 ml.), washed with water, and after being dried (Na_2SO_4), were allowed to evaporate at room temperature. The residue (7·6 g.), after crystallisation from light petroleum, gave 1-*phenyl*cyclo*hexyl hydroperoxide* (6 g.) in long white needles, m. p. 60° (Found : C, 74·5; H, 8·3. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%). Treatment of the product with 15% sulphuric acid (cf. ref. 4) gave *cyclo*hexanone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 159—160°) and phenol (phenyl benzoate, m. p. and mixed m. p. 68°).

Di-(1-*phenyl*cyclo*hexyl*) *Peroxide*.—1-Phenyl*cyclo*hexanol (1·5 g.) and 1-phenyl*cyclo*hexyl-hydroperoxide (0·8 g.) were heated together at 80°. A small crystal of toluene-*p*-sulphonic acid was added to the molten mixture which was maintained at 80° for 5 hr. Methanol (20 ml.) was added and the solid which separated was crystallised from ethanol to give *di*-(1-*phenyl*cyclo*hexyl*) *peroxide* (0·35 g.) in needles, m. p. 123—124° (Found : C, 81·5; H, 8·65. $C_{24}H_{30}O_2$ requires C, 82·2; H, 8·6%). The infrared spectrum showed a strong absorption band at 902 cm.$^{-1}$. Absorption in this region is regarded as being characteristic of the peroxide linkage.[11] Preparation on a larger scale gave considerably lower yields.

1 : 10-*Dibenzoyldecane*.—Decane-1 : 10-dicarboxylic acid (5 g.) was heated under reflux with thionyl chloride (20 ml.) until the evolution of gases ceased. The excess of thionyl chloride was removed under reduced pressure and the pale yellow residue of the acid chloride, dissolved in dry benzene (25 ml.), was added dropwise, with cooling, during 45 min. to a vigorously stirred suspension of aluminium chloride (10 g.) in dry benzene (30 ml.). The mixture was heated to 80° during 30 min. and kept at 80° until no further hydrogen chloride was evolved. After cooling, the mixture was poured on crushed ice (200 g.) and concentrated hydrochloric acid (40 ml.), and chloroform (100 ml.) was added. The organic layer was separated, washed with 10% aqueous potassium hydroxide (2 × 50 ml.), and dried (Na_2SO_4). Chloroform and benzene were distilled off, and addition of light petroleum to the residue then gave a white solid (4·8 g.), m. p. 95°. One crystallisation from benzene–light petroleum gave 1 : 10-*dibenzoyldecane* as plates, m. p. 96—97° (Found : C, 82·0; H, 8·4. $C_{24}H_{30}O_2$ requires C, 82·2; H, 8·6%).

Decomposition of Di-(1-*phenyl*cyclo*hexyl*) *Peroxide*.—(a) *In chlorobenzene*. A solution of di-(1-phenyl*cyclo*hexyl) peroxide (4 g.) in anhydrous chlorobenzene (100 ml.) was boiled under reflux for 6 days. The dark red mixture, when cold, was extracted with 10% aqueous sodium hydroxide (50 ml.) and with saturated aqueous sodium hydrogen sulphite (50 ml.). After being washed with water and dried (Na_2SO_4), the mixture was distilled to remove chlorobenzene, and

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[10] Sabatier and Mailhe, *Compt. rend.*, 1904, **138**, 1322.

[11] Bellamy, " Infra-red Spectra of Complex Molecules," Methuen, London, 1954.

subsequent distillation of the residue gave a pale yellow oil (1·5 g.), b. p. 126°/10 mm., which solidified at 0°, and a residue (2·14 g.), b. p. above 200°/10 mm. The oil contained chlorine (3·5%. Calc. for $C_{12}H_9Cl$: Cl, 18·9%) attributed to traces of residual solvent (cf. the next experiment), and gave a semicarbazone, m. p. 130°, and a 2 : 4-dinitrophenylhydrazone, which after chromatography in benzene on alumina had m. p. 165°. Schroeter[12] reports b. p. 145°/22 mm. for *n*-pentyl phenyl ketone and m. p. 132° for its semicarbazone, but Fahim and Mustapha[13] report *n*-pentyl phenyl ketone as giving a 2 : 4-dinitrophenylhydrazone m. p. 129°. An authentic specimen of *n*-pentyl phenyl ketone (b. p. 140°/15 mm.) was prepared by Schroeter's method and gave a semicarbazone, m. p. 130°, and a 2 : 4-dinitrophenylhydrazone, m. p. 167° (Found: N, 15·3. Calc. for $C_{18}H_{20}O_4N_4$: N, 15·7%). The m. p.s of these derivatives were not depressed on admixture with the corresponding derivatives prepared from the product obtained from the decomposition of the peroxide. The residue, on treatment with light petroleum (80 ml.), yielded a white solid (0·4 g.), m. p. 88—92°. This material consisted of two compounds, one of which crystallised in plates, and the other as rhombs. When these were separated manually, the former had m. p. 92—95°, undepressed on admixture with 1 : 10-dibenzoyldecane, and the latter had m. p. 102—103°, depressed on admixture both with the former compound and with di-(1-phenyl*cyclo*hexyl) peroxide, but gave a precipitate with Brady's reagent. Neither compound could be further purified. Evaporation of the light petroleum mother-liquors yielded an intractable gum. The sodium hydroxide and sodium hydrogen sulphite extracts were acidified with hydrochloric acid and extracted with ether, but evaporation of the extracts in each case yielded only traces of dark products which could not be identified.

(b) *In pyridine.* A solution of di-(1-phenyl*cyclo*hexyl) peroxide (11 g.) in anhydrous pyridine (150 ml.) was boiled under reflux for 2 weeks. The bulk of the solvent was distilled off and chloroform (100 ml.) was added to the dark residue. The solution was extracted with 5N-hydrochloric acid (4 × 25 ml.), washed with water, and dried (Na_2SO_4). The acid extracts were made alkaline with potassium hydroxide and extracted with benzene (5 × 30 ml.). The benzene extracts, after being dried ($CaCl_2$), were distilled. The sole product, however, was a dark tar (0·2 g.), b. p. above 200°/20 mm. The chloroform solution was concentrated and distilled to give a pale yellow oil (2·3 g.), b. p. 148°/22 mm., and a residue (9 g.). The oil gave a semicarbazone, m. p. 130°, and a 2 : 4-dinitrophenylhydrazone, m. p. 166·5°, which did not depress the m. p.s of the corresponding derivatives of *n*-pentyl phenyl ketone. Treatment of the residue with light petroleum gave a white solid (1·1 g.), m. p. 88—92°. A portion of this solid (0·8 g.) was dissolved in benzene (20 ml.) and was poured on an alumina column (25 × 2 cm.). Elution with light petroleum–benzene afforded prisms (0·36 g.) which, after crystallisation from methanol, had m. p. 104·5°, undepressed on admixture with the *substance*, m. p. 102—103°, obtained in the experiment with chlorobenzene (Found: C, 82·7; H, 8·8. $C_{26}H_{34}O_2$ requires C, 82·6; H, 9·0%). The ketone, m. p. 104·5° (0·2 g.), was added to a solution of ammonium acetate (10 g.) in glacial acetic acid (25 ml.) and the mixture was boiled under reflux for 16 hr. The cold mixture was made alkaline with sodium carbonate and was extracted with ether (3 × 30 ml.). The extracts, after being dried (Na_2SO_4), were evaporated to dryness but the dark residue did not contain nitrogen and gave no distinct colour with sulphuric acid. Elution of the column was continued with 1 : 1 benzene–ether to give white plates (0·18 g.), m. p. 96—97°, undepressed on admixture with 1 : 10-dibenzoyldecane. The light petroleum mother-liquors were poured on an alumina column (25 × 2 cm.), and elution with benzene (100 ml.) gave a brown oil (3·7 g.) which, on the addition of methanol (25 ml.), gave a white solid (0·5 g.). Crystallisation of the solid from methanol gave the ketone obtained from the previous chromatography, m. p. and mixed m. p. 104·5°.

Decomposition of 1-*Phenyl*cyclo*hexyl Hydroperoxide in Chlorobenzene.*—1-Phenyl*cyclo*hexyl hydroperoxide (5 g.) in anhydrous chlorobenzene (150 ml.) was boiled under reflux. Decomposition was complete in 60 hr. (negative starch–iodide test) and the cold mixture was extracted successively with 10% aqueous sodium hydroxide (2 × 50 ml.) and with saturated aqueous sodium hydrogen sulphite (2 × 75 ml.). The solution was washed with water and, after being dried (Na_2SO_4), was distilled to remove chlorobenzene. Distillation of the residue gave a yellow oil (2·3 g.), b. p. 126°/8 mm., and a residue (0·7 g.). The oil gave a 2 : 4-dinitrophenylhydrazone (m. p. 158°, from benzene–ethanol), which could not be further purified but

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[12] Schroeter, *Ber.*, 1907, **40**, 1589.

[13] Fahim and Mustapha, *J.*, 1949, 519.

did not depress the m. p. of *n*-pentyl phenyl ketone 2 : 4-dinitrophenylhydrazone. A semicarbazone could not be prepared. No pure product could be obtained either from the residue or from the sodium hydroxide or sodium hydrogen sulphite extracts.

Reaction of 1-*Phenyl*cyclo*hexyl Hydroperoxide with Ferrous Sulphate.*—A saturated ethanolic solution of 1-phenyl*cyclo*hexyl peroxide (4 g.) was slowly added with shaking to a solution of ferrous sulphate (30 g.) in water (70 ml.). An exothermic reaction ensued, which was accompanied by a darkening of the mixture and precipitation of a brown solid. After 2 hr., the mixture was heated to 100° and the solid was dissolved by the addition of 10% sulphuric acid. The solution, when cold, was extracted with methylene chloride (2 × 50 ml.), and the extracts were washed with water and dried (Na_2SO_4). Methylene chloride was distilled off. Addition of methanol (30 ml.) to the residue (3 g.) precipitated 1 : 10-dibenzoyldecane (0·9 g.) which, after crystallisation from benzene–light petroleum, had m. p. and mixed m. p. 96—97°.

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