Reactions of Organic Peroxides. Part X.[1] Amino-peroxides from Cyclohexanone

By **E. G. E. Hawkins**, BP Chemicals Ltd., Research and Development Department, Epsom Division, Great Burgh, Epsom, Surrey

Reaction of cyclohexanone with hydrogen peroxide and ammonia gives either 1,1'-peroxydicyclohexylamine or 1-hydroperoxycyclohexylamine, depending on the ketone to hydrogen peroxide ratio. The reactions of these peroxy-amines studied include (i) base-catalysed conversion of 1,1'-peroxydicyclohexylamine into caprolactam and cyclohexanone, (ii) vapour-phase pyrolysis of 1,1'-peroxydicyclohexylamine to decane-1,10-dicarbonimide, 11-cyanoundecanoic acid, caprolactam, and cyclohexanone, and (iii) conversion of 1-hydroperoxycyclohexylamine into cyclohexanone oxime with tungstate catalysts.

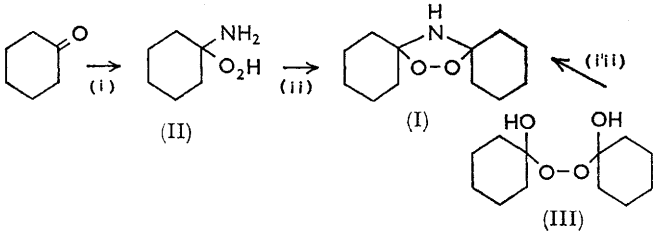
THE catalysed oxidation of cyclohexylamine to cyclohexanone oxime by hydrogen peroxide is known [2-5] and the replacement of cyclohexylamine by cyclohexanone and ammonia in this reaction has been reported more recently; [6-8] in one case [8] a 93% yield of oxime is claimed.

We have found that when solutions of cyclohexanone and hydrogen peroxide (molar ratio *ca.* 2 : 1), generally in aqueous methanol or aqueous ethanol, are saturated with ammonia at 20—40°, the solid peroxide (I) is produced in high yield. Its structure was confirmed by analysis, i.r., n.m.r., and mass spectroscopy (see Experimental Section), and by its reactions. Although the rate of formation of (I) was fairly slow (1—2 days) this time could be cut to a few hours by addition of ammonium or sodium acetate.[9] The peroxide, soluble in all

[1] Part IX, B. Yeomans and D. P. Young, *J. Chem. Soc.*, 1958, 2288.
[2] K. Kahr and C. Berther, *Chem. Ber.*, 1960, **93**, 132.
[3] P. Burchard, J. P. Fleury, and F. Weiss, *Bull. Soc. chim. France*, 1965, 2730.
[4] G.P. 1,190,935 (Ugine).
[5] Belg. P. 659,334 (Halcon).
[6] O. L. Lebedev and S. N. Kazarnovskii, *J. Gen. Chem.*, (*U.S.S.R.*), 1960, **30**, 1635.
[7] B.P. 1,056,124 (I.C.I.).
[8] Fr. P. 1,468,022 (Toa Gosei).
[9] Private communication from Mr. P. Durston.

organic solvents but not in water, is stable to distillation at 15 mm., but decomposes above 150°. It formed monoacetyl and *N*-chloro-derivatives and gave a phenylurea.

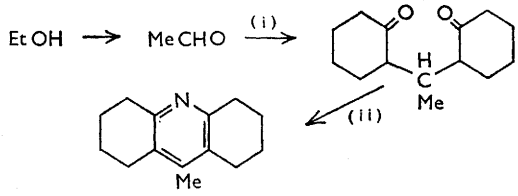
With a ratio of cyclohexanone to hydrogen peroxide at *ca.* 1 : 1 the α-hydroperoxy-amine (II) was rapidly produced (<½ hr.). This hydroperoxide, previously identified, but not isolated, in the ozonolysis of cyclohexylidenecyclohexane in the presence of ammonia,[10] was unstable at room temperature, particularly when impure, but could be stored for several weeks at −20°. The hydroperoxide (II) was evidently an intermediate in the formation of (I):



Reagents: i, NH_3–H_2O_2; ii, cyclohexanone; iii, NH_3

With a deficiency of ammonia in these reactions the major product was 1,1′-dihydroxydicyclohexyl peroxide (III); this could be converted into the peroxy-amine (I) by treatment with ammonia.

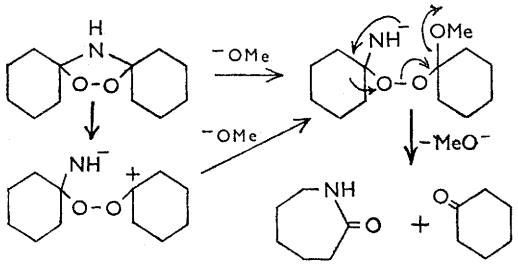
When a methanolic solution of (I) was heated under reflux with sodium methoxide or phenoxide, or an alkali-metal hydroxide, the peroxide was converted, in high yield, into caprolactam and cyclohexanone. Replacement of the sodium methoxide by aqueous alcoholic sodium hydroxide gave ammonia and cyclohexanone with only small amounts of caprolactam whilst the use of organic bases (*e.g.* pyridine) led to slow decomposition of the peroxide and low yields of the lactam; the alkoxides of alkaline-earth metals (calcium or magnesium) and sodamide in benzene were also unsuitable. By-products from the reaction included cyclohex-1-enylcyclohexan-2-one (by base-catalysed self-condensation of the cyclohexanone), traces of caproamide and octahydroacridines. Formation of 9-alkyl-1,2,3,4,5,6,7,8-octahydroacridines increased when higher alkoxide–alkanol systems were used and were then accompanied by cyclohexanol. It seems probable that the octahydroacridines and cyclohexanol arose from Oppenauer oxidation of part of the solvent alkanol to the corresponding carbonyl compound, with simultaneous reduction of cyclohexanone to cyclohexanol; this was followed by condensation of the carbonyl compound with cyclohexanone [11,12] and subsequent reaction of the alkylidene-2,2′-biscyclohexanone with ammonia from the peroxide: [13,14]



Reagents: i, cyclohexanone; ii, NH_3–[O]

Use of sodium isopropoxide–isopropyl alcohol or potassium t-butoxide–t-butyl alcohol gave a more rapid reaction but yields of caprolactam fell to <15%, and part of the nitrogen content of the peroxide was lost as ammonia.[15] With potassium t-butoxide little cyclohexanol was formed but the product contained considerable amounts of higher-boiling condensation products.[15]

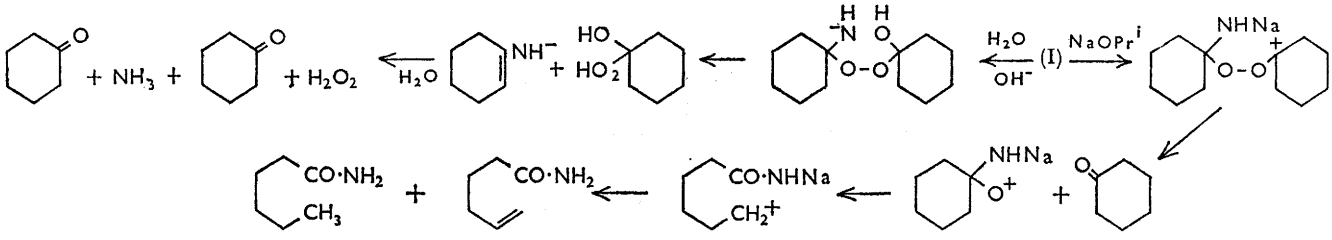
The mechanism of the conversion of the peroxy-amine (I) into caprolactam and cyclohexanone is uncertain. The possibility that the first stage involved removal of the proton from the imino-group, followed by a rearrangement, was eliminated when it was found that *N*-methyl-1,1′-peroxydicyclohexylamine, synthesised by heating the peroxy-amine (I) with methyl iodide and silver carbonate in benzene, gave *N*-methylcaprolactam and cyclohexanone on reaction with sodium methoxide solution. Since a solution of (I) in methanol alone, when heated to *ca.* 100° gave a 40—50% yield of caprolactam, the possibility arises that heat leads to opening of the dioxazolidine ring to give a zwitterion; the presence of base may stabilise the intermediate during rearrangement. Alternatively, a direct nucleophilic attack at C-1 by the methoxy-ion may occur.



One stage in this decomposition would involve a normal Kornblum–de la Mare fission.[16] On the basis of such a mechanism, steric considerations may impede the entry of bulky alkoxy—(*e.g.* isopropoxy) groups and a different

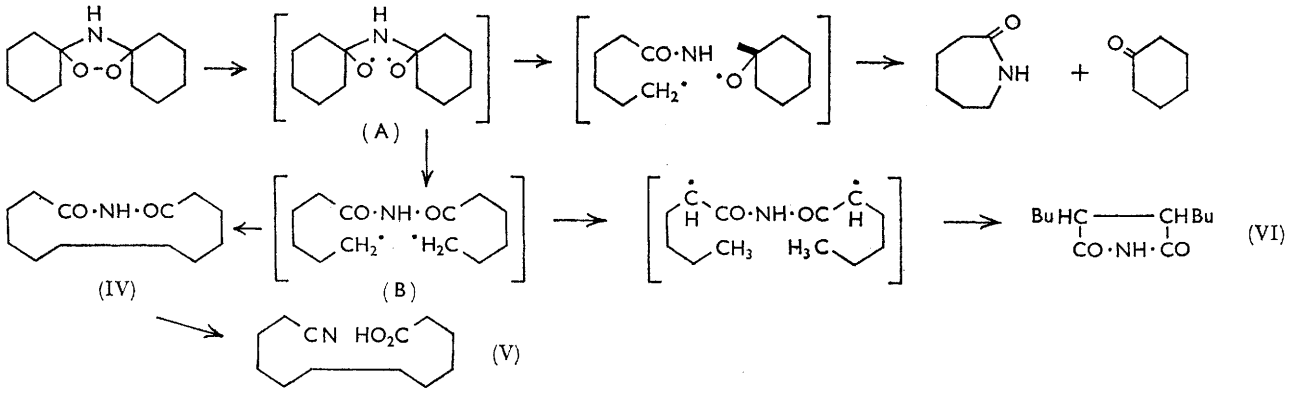
[10] M. Schulz, A. Rieche, and D. Becker, *Chem. Ber.*, 1966, **99**, 3233.
[11] J. Colonge, J. Dreux, and H. Delplace, *Compt. rend.*, 1954, **238**, 1237.
[12] M. N. Tilichenko, *Chem. Abs.*, 1964, **60**, 419.
[13] J. Colonge, J. Dreux, and H. Delplace, *Bull. Soc. chim. France*, 1957, 447.
[14] A. F. McKay, C. Podesva, E. J. Tarlton, and J. M. Billy, *Canad. J. Chem.*, 1964, **42**, 10.
[15] Private communication from Mr. K. W. Denbigh.
[16] N. Kornblum and H. E. De La Mare, *J. Amer. Chem. Soc.*, 1951, **73**, 880.

mode of decomposition, leading to a higher proportion of C_6 amides and cyclohexanone in the product, may occur; *e.g.*



However, further evidence is necessary to confirm or exclude the above hypothesis or to offer alternative possible routes (*e.g.* nucleophilic attack at a peroxidic oxygen atom).

Thermal decomposition of the peroxy-amine (I) in the liquid phase gave a complex mixture of products, including caprolactam, cyclohexanone and C_{12} compounds. However, pyrolysis in the vapour phase at 350—600° under reduced pressure gave *ca.* 60% yields of C_{12} compounds together with caprolactam (*ca.* 20%) and cyclohexanone (<30%). The nature of the C_{12} compounds varied with the temperature and residence time; at 350—400° the major product was decane-1,10-dicarbonimide (IV), and at higher temperatures 11-cyanoundecanoic acid (V), but in addition there were isolated small amounts of 11-carbamoylundecanoic acid and 1,10-dicarbamoyldecane. The imide (IV) was converted into the cyano-acid (V) by repyrolysis at higher temperatures. The formation of the C_{12} compounds involves homolytic decomposition, possibly with radical recombination within a cage; the cyclohexanone and caprolactam arose either from a competing homolytic reaction involving N–C bond fission, or from a base-catalysed heterolytic decomposition. Traces of di-n-butylsuccinimide (VI) identified by spectroscopic methods, were found in material separated by t.l.c. from the neutral, high-boiling product of this pyrolysis.[17] Isomerisation of a radical of type (A) to that of type (B)



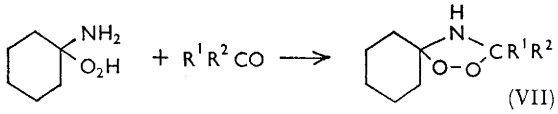
is similar to that occurring with α-methylcyclohexyloxy [18] and α-hydroxycyclohexyloxy [19] radicals.

The imide (IV) was also a major product from the photodecomposition of solutions of the peroxide (I) and caprolactam and cyclohexanone were co-products.

When warmed with acids the peroxy-amine (I) was reconverted into cyclohexanone; formic acid also gave ammonium formate and a small amount of caprolactone, whilst acetic acid–acetic anhydride produced acetamide.

Reaction of the peroxy-amine (I) with a warm ferrous sulphate solution containing sulphuric acid yielded cyclohexanone and caproamide, probably *via* the α-hydroperoxy-amine, which was found to react with ferrous sulphate in the cold. Ferrous chloride and cuprous chloride gave rise to ω-chlorocaproamide. On the other hand, thermal decomposition of the peroxy-amine (I) in the presence of traces of copper naphthenate produced cyclohexanone and hex-5-enoamide.[20]

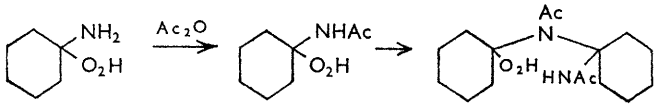
Under all reaction conditions the α-hydroperoxy-amine (II) tended to break down into its components. Thus, although unsymmetrical amino-peroxides were formed on treatment with carbonyl compounds, the crude products always contained some cyclohexanone and, particularly with the less reactive acyclic ketones, *e.g.* acetone, varying amounts of 1,1′-peroxydicyclohexylamine:



Unsymmetrical peroxy-amines (VII) were obtained from acetaldehyde, n-butyraldehyde, acetone, diethyl ketone and dihydroisophorone; that from formaldehyde was too unstable to distil and tended to yield formamide even on storage at room temperature.

[17] Private communication from Dr. A. Hall.
[18] E. G. E. Hawkins and D. P. Young, *J. Chem. Soc.*, 1950, 2804.
[19] E. G. E. Hawkins, *J. Chem. Soc.*, 1955, 3463.
[20] H. E. De La Mare, J. K. Kochi, and F. F. Rust, *J. Amer. Chem. Soc.*, 1963, **85**, 1437.

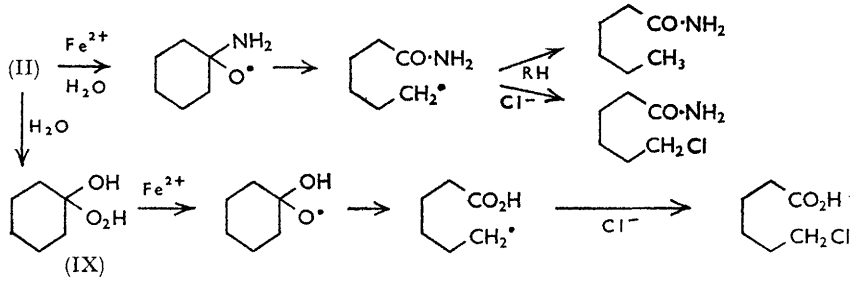
Attempts to acetylate the α-hydroperoxy-amine (II), either with acetyl chloride–triethylamine or acetic anhydride at room temperature, led to the formation of a peroxidic product, m.p. 154—155°, for which the structure (VIII) is proposed on the basis of its active oxygen equivalent, elemental analysis, and spectroscopic properties (mass spectroscopy, n.m.r. and i.r.); such a compound would be derived from the expected *N*-(1-hydroperoxycyclohexyl)acetamide by loss of hydrogen peroxide. If this reaction was carried out at higher



(VIII)

temperatures it provided acetamide and cyclohexanone, evidently by decomposition of (VIII), and cyclohex-1-enyl acetate (by acetylation of cyclohexanone). From the corresponding reaction of the α-hydroperoxy-amine (II) with benzoyl chloride and triethylamine no related product was isolated; instead there were obtained benzoyl peroxide, benzamide, and 1-benzamidocyclohexanol.

Reaction of the peroxide (II) with solutions of ferrous salts was rapid; ferrous sulphate gave cyclohexanone together with small amounts of caproamide and caproic acid, whilst ferrous chloride provided cyclohexanone, ω-chlorocaproamide, and ω-chlorocaproic acid:



(IX)

The formation of ω-chlorocaproic acid is evidence for breakdown of the α-hydroperoxy-amine (II) to cyclohexanone and hydrogen peroxide, which, *via* a 'cyclohexanone peroxide' [*e.g.* (IX)], are known to give ω-chlorocaproic acid on treatment with ferrous chloride.[20] Further evidence is provided by the isolation of dicyclohexylidene peroxide from the products of reaction of a solution of the α-hydroperoxy-amine in sulphuric acid with ferrous sulphate solution.

Pyrolysis of solutions of the hydroperoxide (II) at 450—500°/150 mm. gave products similar to those derived from the symmetrical peroxyamine (I), *i.e.* cyclohexanone, caprolactam, 11-cyanoundecanoic acid, and small amounts of caproamide and cyclohexenylcyclohexanone.

Decomposition of the α-hydroperoxy-amine (II), in aqueous ammonia and ethanol, by catalytic amounts of sodium tungstate or tungstophosphoric acid gave cyclohexanone oxime. Whether the oxime is derived directly from the peroxide by rearrangement or *via* its hydrolysis products is uncertain.

Treatment of the hydroperoxide (II), in cold ethanolic solution, with concentrated sulphuric acid yielded a solid, which, from its analysis, appeared to be a mixture of the monoamine sulphate and diamine sulphate. This sulphate, on warming in aqueous solution, decomposed to give cyclohexanone and small quantities of cyclohexenylcyclohexanone, adipic acid, and caprolactone.

Base-catalysed decomposition of the unsymmetrical amino-peroxide (VII; $R^1 = H$, $R^2 = Me$) gave, as expected for a secondary-tertiary peroxide,[16] mainly cyclohexanone and acetamide, but the rapid reaction with methanolic lithium chloride yielded, in addition, moderate amounts of caprolactam.

EXPERIMENTAL

Preparation of 1,1′-Peroxydicyclohexylamine (I).—(a) *From cyclohexanone.* To a solution of cyclohexanone (90 g.) in a mixture of ammonia (*d* 0·880; 50 c.c.), water (20 c.c.), and methanol (45 c.c.), containing EDTA (sodium salt; 1·0 g.), was gradually added 30% hydrogen peroxide (70 c.c.) at *ca.* 20°. The solution was saturated with gaseous ammonia and stored at room temperature for 48 hr. The crystalline *1,1′-peroxydicyclohexylamine* (I) was purified by distillation; the peroxide (75·7 g.), had b.p. 94—97°/0·4 mm., 130—140°/15 mm., m.p. 40—42° (from light petroleum or aqueous ethanol) [Found: C, 68·0, 68·2; H, 10·0, 9·9; N, 6·5%; active O equiv., 210; amine equiv., (by perchloric acid–acetic acid), 211. $C_{12}H_{21}NO_2$ requires C, 68·2; H, 9·95; N, 6·6%; active O and amine equiv. 211]. By mass spectroscopy it gave a molecular ion, *m/e* 211 ($C_{12}H_{21}NO_2$), and an ion $C_{12}H_{21}N$ ($-O_2$). Its n.m.r. spectrum showed ring methylenic protons (τ 8·14—8·87) and deuterium-replaceable protons (τ 7·6) in the ratio of 20 : 1, and i.r. spectroscopy indicated secondary amine absorption at 3300 $cm.^{-1}$.

(b) *From 1,1′-dihydroxydicyclohexyl peroxide* (III). The peroxide (26·5 g.), water (35 c.c.), ammonia (*d* 0·880; 12·5 c.c.), and EDTA (sodium salt; 0·2 g.) were mixed and stored at 0° for 1 week. The crystalline mass was extracted with ether and the extract was distilled to provide peroxyamine (17·5 g.).

(c) *From Cyclohexanol Autoxidate.* Cyclohexanol (125 c.c.), (which had been oxygenated at 115—124° for 8½ hr. and contained 0·08 mole of active oxygen) mixed with cyclohexanone (33 g.) was saturated with gaseous ammonia and stored at room temperature for 3 days. The solution was diluted with water and extracted with light petroleum. Distillation of the extract yielded a peroxy-amine fraction (9·8 g.), b.p. 100—114°/1·0 mm., which crystallised on storage.

Preparation of 1-*Hydroperoxycyclohexylamine* (II).—Hydrogen peroxide (30%; 70 c.c.) was added to a stirred, cooled mixture of cyclohexanone (49 g.), methanol (30 c.c.), ammonia (*d* 0·880; 55 c.c.) and EDTA (sodium salt; 0·5 g.) and the temperature was maintained at <25° for 1 hr.; the solid 1-hydroperoxycyclohexylamine (57 g.) was washed with cold water and light petroleum and dried. The dried solid recrystallised from acetone gave 1-*hydroperoxycyclohexylamine*, m.p. 57—58° (decomp.) (Found: C, 55·1; H, 9·85; N, 10·9%; active oxygen equiv., 137; amine equiv., 135. $C_6H_{13}NO_2$ requires C, 54·95; H, 9·95; N, 10·7%; active oxygen and amine equiv., 131). The spectroscopic examination of this compound could not be carried out owing to (*a*) its insolubility in suitable solvents, and (*b*) the rapidity of its decomposition at room temperature.

Preparation of N-*Methyl*-1,1′-*peroxydicyclohexylamine*.—Peroxy-amine (I) (36 g.), methyl iodide (50 g.), silver carbonate (60 g.), and benzene (100 c.c.) were heated together under reflux for *ca.* 70 hr. During this time further methyl iodide (4 × 25 g.) and silver carbonate (40 g.) were added. The filtered product was distilled and suitable cuts were redistilled through a small column to provide the *N*-methylperoxy-amine (5·0 g.), b.p. 95—98°/0·4 mm.; 90—95% pure by i.r. spectroscopy. An aqueous alcoholic solution of this distillate when cooled gave N-*methyl*-1,1′-*peroxydicyclohexylamine*, m.p. 33—35° (Found: C, 68·8; H, 10·25; N, 6·1%; active oxygen equiv., 222·5. $C_{13}H_{23}NO_2$ requires C, 69·3; H, 10·2; N, 6·2%; active oxygen equiv., 225); the i.r. spectrum was in agreement with the formulation.

Reaction of 1,1′-*Peroxydicyclohexylamine with Bases*.—(a) *With sodium methoxide*. A solution of the peroxy-amine (10 g.) in methanol (10 c.c.) was added to a solution of sodium (2 g.) in methanol (30 c.c.), and the mixture was heated under reflux for 1½ hr., when <5% of the peroxide remained. The cooled solution was diluted with water, neutralised with hydrochloric acid (Congo red), and extracted with chloroform. The extract, on distillation, gave cyclohexanone (4·7 g.) and a caprolactam fraction (4·2 g.), 93% pure by i.r. spectroscopy, but containing some cyclohexenylcyclohexanone. Pure caprolactam, m.p. and mixed m.p. 68—70°, was isolated on crystallisation from benzene–light petroleum.

(b) *With sodium ethoxide*. Reaction (½ hr.) as in (a), with replacement of methanol by ethanol gave the following upon distillation at 15 mm.: (i) (2·3 g.), b.p. 40—130°; (ii) (4·0 g.), b.p. 130—175°; (iii) (2·6 g.), b.p. 175—240°; and residue (0·6 g.). By i.r. spectroscopy fr. (i) was cyclohexanol containing 20% of cyclohexanone and caprolactam (5%); fr. (ii) was 80% caprolactam with cyclohexenylcyclohexanone; and fr. (iii) contained caprolactam, amide and acid, and a substituted pyridine. From fr. (iii) was isolated, by trituration with ether, a solid, m.p. 234—238° (from EtOAc–EtOH) (Found: C, 69·7; H, 8·4; N, 6·0. $C_{14}H_9N$,HCl requires C, 70·7; H, 8·5; N, 5·9%), shown to be 9-*methyl*-1,2,3,4,5,6,7,8-*octahydroacridine hydrochloride* by i.r., n.m.r., and mass spectroscopy. The free base, m.p. 44—46°, was liberated by treatment of the hydrochloride with aqueous ammonia, and both this and the hydrochloride were identical with the synthetic compounds obtained by heating ethylidene-2,2′-biscyclohexanone [12] with ammonium nitrate.

(c) *With other bases*. The peroxyamine (10 g.) heated with other bases in methanol, gave yields of products as in the Table.

Base	Wt. (g.)	Vol. of methanol (c.c.)	Reflux time (hr.)	Cyclohexanone (g.)	Caprolactam (g.)
Bu^nONa	8·3	35	1½	2·2	4·5
PhONa	11·0	40	6¼	1·8	3·0
NaOH	3·5	40	2¼	3·7	3·6

Peroxy-amine (0·0947 mole) heated with sodium isopropoxide (0·178 mole) in isopropyl alcohol at 90° for 1 hr. gave molar yields: ammonia (48%), cyclohexanone (30·4%), cyclohexanol (102%), caprolactam (8·8%), n-caproamide and hex-5-enoamide (8%), caproic acid (18·2%), and high boiling materials (9·5% w/w).[15]

Reaction of N-*Methyl*-1,1′-*peroxydicyclohexylamine with Sodium Methoxide*.—The peroxide (90—95% pure; 2·5 g.) was added to a solution of sodium (0·5 g.) in methanol (10 c.c.) and the mixture was heated under reflux for 1¾ hr. The solution was worked up to give cyclohexanone (1·0 g.), *N*-methylcaprolactam (0·9 g.), caprolactam (<0·1 g.), and residue (0·2 g.). The *N*-methylcaprolactam was identified by i.r. (1650 $cm.^{-1}$; CO stretch of t-amide), n.m.r. and mass [*m/e* 127 ($C_7H_{13}NO$)] spectroscopy.

Thermal Decomposition of 1,1′-*Peroxydicyclohexylamine*. *In boiling* β-*picoline*. The peroxy-amine (I) (8 g.) was heated with refluxing β-picoline (20 g.) for 2½ hr.; no peroxide then remained. Distillation gave β-picoline, containing cyclohexanone, fractions (1·6 g.) consisting largely of caprolactam, and a fraction (2·2 g.), b.p. 250—260°/15 mm., which crystallised in the receiver. The last fraction was separated into acid and neutral portions by treatment with sodium hydroxide. The neutral portion, m.p. 193—195° (from ethanol) (Found: C, 62·75; H, 10·55; N, 12·1. Calc. for $C_{12}H_{24}N_2O_2$: C, 63·1; H, 10·6; N, 12·25%) was found to be the diamide of dodecane-1,12-dioic acid by comparison with synthetic material prepared by treatment of the C_{12} acid chloride with ammonia.[21] The acid portion, m.p. 132—134° (from EtOAc) (Found: C, 62·8; H, 9·7; N, 5·9. Calc. for $C_{12}H_{23}NO_3$: C, 62·9; H, 10·0; N, 6·1) was 11-carbamoylundecanoic acid, identical (m.p. and spectra) with the synthetic material. Both of these products yielded dodecane-1,12-dioic acid, m.p. and mixed m.p. 127·5—129°, on hydrolysis with aqueous alcoholic sodium hydroxide.

Vapour-phase pyrolysis. (i) The peroxy-amine (8 g.) in pyridine (20 c.c.) was dropped into a column, packed with glass beads (6 in.), at 375°, during 40 min. The pyrolysis was carried out at 150 mm. in a slow stream of nitrogen. Solvent was removed and the residue was triturated with light petroleum to yield a solid (4·0 g.). Recrystallisation from ethanol provided *decane*-1,10-*dicarbonimide*, m.p. 136—137° (Found: C, 67·9; H, 10·0; N, 6·5. $C_{12}H_{21}NO_2$ requires C, 68·2; H, 9·95; N, 6·65%); i.r. spectroscopy showed the presence of the CO·NH·CO group, and mass spectroscopy indicated a molecular ion $C_{12}H_{21}NO_2$. When warmed with aqueous ethanolic sodium hydroxide, followed by acidification, the imide yielded 11-carbamoylundecanoic acid, m.p. 133—135°, undepressed on admixture with that obtained above.

The filtrate from the solid imide was distilled to give: cyclohexanone (0·8 g.), a fraction (1·0 g.) containing 30% caprolactam and some caproamide, and a fraction (1·1 g.) containing caprolactam and compounds with functional groups CO_2H, $CO{\cdot}NH_2$, CN.

(ii) The peroxy-amine (8 g.), dissolved in ethanol (40 c.c.) was dropped into the same column as above, but at 590°/15

[21] C. R. Barnicoat, *J. Chem. Soc.*, 1927, 2926.

mm. during 1 hr. Distillation gave cyclohexanone, a fraction (1·2 g.) containing caprolactam (50%) and unchanged peroxy-amine, a fraction (5·0 g.), b.p. 170—275°/15 mm., and residue (0·4 g.). The last fraction crystallised on storage, and recrystallisation from light petroleum provided 11-cyanoundecanoic acid, m.p. 56—58° (lit.,[22] m.p. 57°) (Found: C, 68·05; H, 10·1; N, 6·7. Calc. for $C_{12}H_{21}NO_2$: C, 68·2; H, 9·95; H, 6·65%). Alkaline hydrolysis yielded 1,12-dodecanedioic acid, m.p. and mixed m.p. 127·5—129°. From the neutral part of this fraction there was separated, by t.l.c., a small quantity of a compound identified as 1,2-di-n-butylsuccinimide by spectroscopic comparison with synthetic material.

(iii) The peroxy-amine (8 g.), dissolved in ethanol (40 c.c.), was pyrolysed as above at 400°/150 mm. during ½ hr. The high-boiling fraction (5·5 g.) contained (by i.r. spectroscopy) the imide (50%) and cyano-acid (36%).

(iv) The imide (3 g.) in pyridine (10 c.c.) was pyrolysed at 510°/15 mm. during ¾ hr. From the product there were isolated, by crystallisation, unchanged imide (1·6 g.) and cyano-acid (1·1 g.).

Photosensitised Decomposition of 1,1′-Peroxydicyclohexylamine.—A solution of the peroxy-amine (I) (15 g.) and benzophenone (0·1 g.) in benzene (125 c.c.) was irradiated with a mercury-vapour lamp in a Hanovia photochemical quartz reactor for 5¾ hr. at room temperature. No peroxide then remained. The solvent was removed and the residue was treated with light petroleum. Impure decane-1,10-dicarbonimide (4·3 g.) was filtered off and the filtrate was distilled at 14 mm. to give fractions: (i) (2·9 g.), b.p. 138—160°; (ii) (2·15 g.), b.p. 160—210°; (iii) (1·6 g.), b.p. 210—282°; and residue (1·9 g.); by i.r. spectroscopy fr. (i) contained caprolactam (50—60%) in addition to a carboxylic acid and other carbonyl compounds; fr. (ii) was a complex mixture containing caprolactam, decanedicarbonimide, and 11-cyanoundecanoic acid; fr. (iii) had *ca.* 60% of 11-cyanoundecanoic acid, some of the imide and other carbonyl functions.

Rather similar results were obtained with ethanol or pyridine as solvent; an acetic acid solution of the peroxy-amine decomposed very slowly.

Other Reactions of 1,1′-Peroxydicyclohexylamine.—(a) *With Acids.* (i) Formic acid. The peroxide (8 g.) was added to formic acid (10 g.); a vigorous exothermic reaction took place, and after ½ hr. distillation of the product gave fractions containing formic acid, cyclohexanone, 6-hexanolactone (by i.r. spectroscopy), and ammonium formate, m.p. and mixed m.p. 112—114° (isolated by trituration with chloroform).

(ii) *Acetic acid.* A solution of the peroxide (8 g.) in acetic acid (25 c.c.), stirred at 45—50°, was gradually treated with a mixture of acetic acid (10 c.c.) and acetic anhydride (8 g.). The temperature was raised to 80° and stirring was continued for 4 hr.; the peroxide content fell to *ca.* 10% of the original. Distillation gave, in addition to solvent, cyclohexanone (3·5 g.), fractions (ii) (2·0 g.), b.p. 80—125°/15 mm.; (iii) (1·1 g.), b.p. 130—170°/15 mm.; and residue (0·9 g.). By i.r. spectroscopy, fr. (ii) contained acetamide, caprolactone, and acetylated compounds; trituration with ether provided acetamide. By mass spectroscopy fr. (iii) was shown to contain caprolactam and acetylated compounds (including possibly *N*-acetylcaprolactam).

(iii) *Sulphuric acid.* A mixture of the peroxide (10 g.), water (30 c.c.), ethanol (20 c.c.), and sulphuric acid (0·2 c.c.) was heated under reflux for 4½ hr. Ammonia was evolved. The product was extracted with chloroform and the extract distilled to yield cyclohexanone (7·8 g.), unchanged peroxy-amine (0·3 g.) and residue (0·3 g.).

(b) *With Ferrous Sulphate.* To a stirred solution of ferrous sulphate ($FeSO_4,7H_2O$; 20 g.) in water (50 c.c.) and ethanol (50 c.c.) was added a solution of peroxy-amine (10 g.) in ethanol (10 c.c.). Reaction was extremely slow at 5—10°, but proceeded at 20—25°. After 3½ hr. a mixture of sulphuric acid (5 g.) and water (20 c.c.) was added and the solution was extracted with chloroform. Distillation of the extract yielded cyclohexanone (7·0 g.), a fraction (1·8 g.), b.p. 140—150°/15 mm., and residue (1·0 g.). The distilled fraction afforded n-caproamide, m.p. and mixed m.p. 100—101°. Recrystallisation of the residue from ethanol provided 1,10-dicarbamoyldecane.

(c) *With Ferrous Chloride.* A solution of the peroxy-amine (8 g.) in ethanol (10 c.c.) was added to a stirred solution of ferrous chloride (12 g.) in water (20 c.c.) and concentrated hydrochloric acid (10 c.c.) at <30°. After ½ hr. the temperature was raised to 50° and stirring was continued for a further ½ hr. Distillation of the chloroform extract gave cyclohexanone (4·9 g.), and left a solid residue (3·8 g.) which afforded ω-chlorocaproamide, m.p. and mixed m.p. 104—106° (from ethanol).

(d) *With Cuprous Chloride.* As in (c), but with cuprous chloride (10 g.) in place of ferrous chloride, yielded cyclohexanone (5·5 g.) and ω-chlorocaproamide (0·6 g.).

(e) *With Copper Naphthenate.* A mixture of the peroxide (2 g.) and copper naphthenate (0·1 g.) was heated to 110—120°, and the product was distilled to give cyclohexanone (0·8 g.), a fraction (0·2 g.), b.p. 140—150°/14 mm., and residue (1·0 g.). The distilled fraction yielded ω-hexenoamide, m.p. 85—86° (from light petroleum), identified by i.r. and mass spectroscopy.

(f) *With Acetyl Chloride.* To a cooled, stirred solution of peroxide (20 g.) in ether (100 c.c.) and triethylamine (15 g.) was gradually added acetyl chloride (12 g.) in ether (20 c.c.); the temperature was <10°. The mixture was stored at room temperature overnight, diluted further with ether, washed, with water, dilute sodium hydroxide solution and water; the ethereal solution was dried and distilled to give: (i) unchanged peroxide (12·0 g.); (ii) a fraction (2·7 g.), b.p. 120—150°/1·0 mm., containing the peroxy-amine and its acetylated derivative; and (iii) a fraction (1·3 g.), b.p. 150°/0·7 mm., which crystallised on storage and provided N-*acetyl*-1,1′-*peroxydicyclohexylamine*, m.p. 123—125° (from light petroleum) (Found: N, 5·2; $C_{14}H_{23}NO_3$ requires N, 5·5%). Its i.r. spectrum indicated a tertiary amide and its mass spectrum showed a molecular ion *m/e* 253, with fragment ions *m/e* 221 (loss of O_2), 178 (loss of O_2 and acetyl), and 43 (acetyl).

(g) *With Phenyl Isocyanate.* Phenyl isocyanate (2·5 g.) was added to a solution of the peroxide (5 g.) in light petroleum (25 c.c.) and the mixture was stored at room temperature, with moisture excluded, for 3 days. Recrystallisation of product provided N-(1,1′-*peroxydicyclohexyl*)-N′-*phenylurea*, m.p. 203—204° (decomp.) (from acetone) (Found: C, 69·0; H, 8·0; N, 8·4%; active oxygen equiv., 331. $C_{19}H_{26}N_2O_3$ requires C, 69·1; H, 7·9; N, 8·5%; active oxygen equiv., 330).

This derivative was also obtained by carrying out the reaction under reflux.

[22] G. A. Perkins and A. P. Cruz, *J. Amer. Chem. Soc.*, 1927, **49**, 1070.

(h) *With t-Butyl Hypochlorite.* t-Butyl hypochlorite (22 g.) in benzene (50 c.c.) was added to a cooled (<7°), stirred solution of the peroxy-amine (42 g.) in benzene (50 c.c.), and stirring was continued for 1 hr. after the addition. The benzene and t-butanol were removed and the residue (49 g.) twice crystallised from ethanol gave *N-chloro-1,1′-peroxydicyclohexylamine,* m.p. 26—28° (Found: C, 58·8; H, 8·25; Cl, 14·4; N, 5·65%; active oxygen equiv., 124·4. $C_{12}H_{20}ClNO_2$ requires C, 58·65; H, 8·15; Cl, 14·45; N, 5·7%; active oxygen equiv., 122·7), having i.r. and n.m.r. spectra in agreement with the suggested structure.

(i) *Catalytic Hydrogenation.* (i) A solution of peroxide (5 g.) in ethanol (50 c.c.), containing 5% palladium-on-charcoal (0·4 g.) was shaken with hydrogen at room temperature; after 5 hr. 1500 c.c. of hydrogen had been absorbed. The filtered solution was distilled to give dicyclohexylamine (3·0 g.), b.p. 108—118°/15 mm., (identified by i.r. spectroscopy).

(ii) Peroxide (5 g.) in ether (25 c.c.), containing 5% palladium-on-charcoal (0·4 g.), was stirred in hydrogen at 0°. After 4 hr. 570 c.c. of hydrogen had been absorbed. The filtered solution smelt strongly of ammonia, and distillation gave cyclohexanone (3·4 g.).

Reactions of 1-Hydroperoxycyclohexylamine.—(a) *With Carbonyl Compounds.* (i) Acetaldehyde. The peroxide (13·1 g.) was added in portions to a cooled, stirred solution of acetaldehyde (5·4 g.) in water (10 c.c.), and the solution was stored at 0° overnight. The product was extracted with ether and the extract was distilled to provide cyclohexanone and the following fractions at 0·5 mm. (wt.; b.p.; peroxide equiv.; amine equiv.): (i) (2·9 g.), 20—50°; 278; 303; (ii) (2·3 g.), 50—55°; 156; 236; (iii) (3·3 g.), 55—65°; 156; 218. Fractions (ii) and (iii) were combined and redistilled to give *1,1′-peroxycyclohexylethylamine,* b.p. 54°/0·25 mm. (Found: peroxide equiv., 157; amine equiv., 165. $C_8H_{15}NO_2$ requires equiv., 157); *phenylurea derivative,* m.p. 147·5—148·5° (from acetone) (Found: C, 65·15; H, 7·3; N, 9·9%; peroxide equiv., 264·3; $C_{15}H_{20}N_2O_3$ requires C, 65·2; H, 7·2; N, 10·15%; peroxide equiv., 264). The peroxycyclohexylethylamine showed secondary-amine absorption in its i.r. spectrum, and by mass spectroscopy it gave a molecular ion *m/e* 157, and a strong ion *m/e* 125 ($C_6H_{10}N{=}CHMe$) (loss of O_2).

(ii) n-Butyraldehyde. Under similar conditions reaction of the peroxide (13·1 g.) with n-butyraldehyde (7·2 g.) gave a fraction (8·4 g.), b.p. 89°/0·3 mm., peroxide equiv., 204, amine equiv., 206, shown to be impure *1,1′-peroxycyclohexyl-n-butylamine* by mass spectroscopy; although the molecular ion (*m/e* 185) and that (153) due to loss of O_2 were present, ions *m/e* 211 and 179 due to 1,1′-peroxydicyclohexylamine were also visible in the spectrum. It provided a *phenylurea derivative,* m.p. 151—152° (decomp.) (from acetone) (Found: C, 66·85; H, 7·9; N, 9·35%; peroxide equiv., 301. $C_{17}H_{24}N_2O_3$ requires C, 67·1; H, 7·9; N, 9·2%; peroxide equiv., 304).

(iii) Acetone. From acetone (10·8 g.) and peroxide (14·1 g.) were obtained a fraction (5·6 g.), b.p. 56—70°/0·3 mm., and a fraction (3·5 g.), b.p. 70—90°/0·3 mm., consisting largely of 1,1′-peroxydicyclohexylamine. The first of these two fractions was redistilled to provide *1,2′-peroxycyclohexylprop-2′-ylamine,* b.p. 56—61°/0·4 mm. (Found: C, 63·15; H, 9·95; N, 7·45%; peroxide equiv., 174·9; amine equiv., 174·6. $C_9H_{17}NO_2$ requires C, 63·15; H, 9·9; N, 8·2%; peroxide and amine equiv., 171); *phenylurea derivative,* m.p. 161—163° (from acetone–ether) (Found: C, 66·3; H, 7·55; N, 9·4. $C_{16}H_{22}N_2O_3$ requires C, 66·2; H, 7·6; N, 9·65%).

(iv) Diethyl ketone. Diethyl ketone, treated as before, gave a product, b.p. 82—84°/0·15 mm. (peroxide equiv., 221; amine equiv., 208·8), shown by n.m.r. and mass spectroscopy to consist of a mixture of 1,3′-peroxycyclohexylpent-3′-ylamine and 1,1′-peroxydicyclohexylamine in a ratio of *ca.* 3 : 1.

(v) Cyclohexanone. Cyclohexanone (9·8 g.) and peroxide (13·1 g.), treated as above, provided 1,1′-peroxydicyclohexylamine (12·5 g.) m.p. and mixed m.p. 39·5—40·5° (from light petroleum).

(vi) Dihydroisophorone. Dihydroisophorone (14·0 g.) and peroxide (13·1 g.) similarly gave (i) fractions (12·2 g.) containing cyclohexanone and dihydroisophorone and (ii) a fraction (8·1 g.), b.p. 100—114°/0·7 mm., (peroxide equiv., 236; amine equiv., 245), shown by i.r. and mass spectroscopy to consist of a mixture of approximately equal parts of 1,1′-peroxydicyclohexylamine and 3,3,5-trimethyl-1,1′-peroxydicyclohexylamine.

(b) *With Acetyl Chloride.* To a stirred, cooled mixture of peroxide (13·1 g.), ether (100 c.c.), and triethylamine (32 g.) was gradually added acetyl chloride (19·6 g.); the solution was kept at 10—15° throughout the addition, and was then stored at room temperature overnight. It was then washed with water and the ethereal extract was dried and evaporated. The semicrystalline residue (8·4 g.), on trituration with light petroleum, yielded the *peroxy-amide* (VIII), m.p. 153° (from ethanol) (Found: C, 62·0; H, 9·0; N, 8·8%; peroxide equiv., 308. $C_{16}H_{28}N_2O_4$ requires C, 61·5; H, 9·0; N, 9·0%; peroxide equiv., 312). Its i.r. spectrum had a band due to secondary amide, its mass spectrum showed the parent ion *m/e* 312 ($C_{16}H_{28}N_2O_4$), and its n.m.r. spectrum was in agreement with the formulation (VIII) [τ 8·53 (12H, β- and α-CH_2 in rings); 8·0 (8H, α-CH_2 in rings), 8·04 (6H, CH_3CO), 3·6 (2H, OH and NH)].

(c) *With Acetic Anhydride.* To acetic anhydride (40 c.c.) was gradually added, with cooling, the peroxide (10 g.). The solution was divided into two equal parts; one part was maintained at room temperature for 6½ hr. and the second part was heated on a water-bath until no peroxide remained (1¾ hr.).

The first part, showing no loss of peroxide, was poured into cold water, neutralised with cold sodium hydroxide solution, and extracted with ether. After evaporation of the solvent the solid residue (6·5 g.) was recrystallised from ether–light petroleum to give the peroxy-amide (VIII), m.p. and mixed m.p. 154—155°, peroxide equiv., 308. When cooled the filtrate gave more of this compound, but further strong cooling gave solid which detonated in the m.p. tube and was thought to be acetyl peroxide.

The heated portion was distilled to provide acetic acid, acetic anhydride, and cyclohexanone (0·8 g.), fractions (2·7 g.) having an αβ-unsaturated ester and a primary amide (by i.r. spectroscopy), and residue (1·3 g.). From the distillate, by trituration with ether, was isolated acetamide, m.p. and mixed m.p. 80—81°.

(d) *With Benzoyl Chloride.* Benzoyl chloride (8 g.) was added gradually to a cooled, stirred mixture of peroxide (7 g.) and 2N-sodium hydroxide (25 c.c.) at <15°. After being stirred for a further 10 mins. the product was extracted with ether. Evaporation of the solvent left a semi-

solid residue, which provided a non-peroxidic solid, m.p. 103—104° (from ethanol–ethyl acetate) (Found: C, 70·6; H, 7·8; N, 6·15. Calc. for $C_{13}H_{17}NO_2$: C, 71·2; H, 7·75; N, 6·4%), identified as 1-benzamidocyclohexanol by i.r. and n.m.r. spectroscopy. The filtrate from the above was evaporated to dryness and the residue was crystallised from light petroleum to give benzoyl peroxide, m.p. and mixed m.p. 105—106°.

(e) *With Ferrous Sulphate.* (i) Peroxide (13 g.) was added gradually to a stirred solution of crystalline ferrous sulphate (32 g.) in water (75 c.c.) at <5°; an exothermic reaction occurred. After 2 hr. the solution was allowed to warm to room temperature and was then extracted with ether. The extract, on distillation, gave cyclohexanone (4·8 g.) and fractions (total wt. 0·9 g.) shown, by i.r. spectroscopy to contain caproic acid and caproamide, together with a small quantity of a secondary amide.

(ii) The sulphate of the hydroperoxy-amine (see below) (10 g.) was stirred with a solution of ferrous sulphate (30 g.) in water (50 c.c.) for 2 hr. at <10°. Solid (0·3 g.), m.p. 130°, undepressed on admixture with dicyclohexylidene peroxide, was filtered off and the filtrate was extracted with ether to provide cyclohexanone (1·4 g.).

(f) *With Ferrous Chloride.* Peroxide (26 g.) was gradually added to a solution of ferrous chloride ($FeCl_2,4H_2O$; 40 g.) in water (50 c.c.) and concentrated hydrochloric acid at <0°. The mixture was stirred for ½ hr. and the temperature was allowed to rise to that of the room. Distillation of the chloroform extract yielded cyclohexanone (13·8 g.), a fraction (2·0 g.), b.p. 155—180°/15 mm., and residue (1·0 g.). The fraction was shaken with sodium hydroxide solution to separate it into acidic and neutral fractions, and yielded ω-chlorocaproamide (from ethyl acetate), m.p. and mixed m.p. 104—106° and ω-chlorocaproic acid, b.p. 142—143°/13 mm., identified by i.r. spectroscopy.

(g) *Pyrolysis.* A solution of the peroxide (23·5 g.) in ethanol (125 c.c.) was pumped into a heated tube packed with glass beads, at 500°/150 mm., during 1 hr. Distillation at 12 mm. gave the following fractions: (i) (2·3 g.), b.p. 40—60°; (ii) (6·5 g.), b.p. 160—190°; (iii) (6·1 g.), b.p. 225—240°; (iv) (0·75 g.), b.p. 240—280°; and residue (1·3 g.). Fraction (i) was mainly cyclohexanone; fr. (ii), separated by g.l.c., was shown to contain cyclohexanone (12·5%), caproamide (3·5%), caprolactam (38·1%), cyclohexenylcyclohexanone (1·8%), and a number of unidentified peaks; fr. (iii) consisted largely of 11-cyanoundecanoic acid, part (4·2 g.) of which was isolated pure by removal from the fraction with alkali; and fr. (iv) contained the cyano-acid and a secondary amide (by i.r. spectroscopy).

(h) *With Tungstophosphoric Acid.* The catalyst (P_2O_5,-$24WO_3,xH_2O$; 3·5 g.), EDTA (sodium salt, 0·2 g.), ammonia (*d* 0·880; 50 c.c.) and ethanol (10 c.c.) were stirred together at room temperature and the peroxide (16 g.) was added gradually. After 2 hr. <10% of the peroxide remained; the solution was extracted with chloroform and the extract was distilled to provide cyclohexanone (2·8 g.) and a fraction (5·3 g.), b.p. 100—110°/15 mm., containing cyclohexanone (10%) and cyclohexanone oxime (90%) (by i.r. spectroscopy); crystallisation (from light petroleum) afforded the oxime, m.p. and mixed m.p. 89—91°.

A qualitatively similar result was obtained when using sodium tungstate as catalyst.

(i) *With Sulphuric Acid.* (i) Treatment of a strongly cooled solution of the peroxide in ethanol with concentrated sulphuric acid gave a white solid, m.p. 131° (decomp.) (Found: C, 33·1; H, 7·2; N, 8·6; S, 12·05; SO_4, 32·8%; peroxide equiv., 222. $C_6H_{15}NO_6S$ requires C, 31·5; H, 6·55; N, 6·1; S, 14·0; SO_4, 41·9%. $C_{12}H_{28}N_2O_8S$ requires C, 40·0; H, 7·8; N, 7·8; S, 8·9; SO_4, 26·65%.

(ii) Peroxide (13·1 g.) was added to water (60 c.c.) containing sulphuric acid (3 drops) and the mixture was heated on a water-bath for 25 min. An exothermic reaction occurred and ammonia was liberated. The product was extracted with ether and this extract, on distillation, provided cyclohexanone (3·5 g.) and a fraction (0·2 g.), b.p. 120—130°/11 mm., shown to be mainly cyclohexenylcyclohexanone by i.r. spectroscopy. The aqueous phase was neutralised and evaporated to dryness; the residue was extracted with ethanol, filtered, and the extract was distilled at 18 mm. to give fractions: (i) (0·45 g.), b.p. 120—140°; (ii) (1·0 g.), b.p. 160—180°; and residue (1·4 g.; water-soluble). By i.r. spectroscopy fr. (i) consisted largely of caprolactone, but also contained adipic acid and a primary amide; fr. (ii) had less caprolactone and more of the acid and amide.

Base-catalysed Decomposition of 1,1′-Peroxycyclohexylethylamine.—(a) *With Triethylamine.* The peroxy-amine (6·5 g.) and triethylamine (10 g.) were heated together under reflux for ½ hr.; little peroxide remained. Distillation gave cyclohexanone (2·7 g.) and a fraction (2·5 g.), b.p. 100—110°/15 mm., which afforded acetamide, m.p. and mixed m.p. 79—81°.

(b) *With Sodium Methoxide.* Peroxide (10 g.) was added gradually to a refluxing solution of sodium (2 g.) in methanol; a vigorous reaction occurred and no peroxide remained at the end of the addition. The cooled solution was diluted with water and extracted with chloroform. Distillation of the extract at 15 mm. gave cyclohexanone (3·3 g.); fr. (ii) (0·5 g.), b.p. 120—160°; fr. (iii) (1·0 g.), b.p. 160—210°, and residue (0·6 g.).

The major components of the higher-boiling fractions were separated by g.l.c. and examined by i.r. and mass spectroscopy. Fr. (ii) contained cyclohexanone (20—30%), acetamide (*ca.* 5%), and a compound thought to be 1-acetyl-1-methoxycyclohexane (30—50%); fr. (iii) consisted mainly (*ca.* 70%) of a mixture of octahydroacridine and 9-methyloctahydroacridine (ratio 1 : 2).

(c) *With Lithium Chloride in Methanol.* Peroxide (9 g.) in methanol was added to a refluxing solution of lithium chloride (10 g.) in methanol (total volume, 40 c.c.). The solution darkened and no peroxide remained after the end of the addition. Work up as before gave, on distillation at 15 mm.: cyclohexanone (3·5 g.); fr. (ii) (0·6 g.), b.p. 120—170°; fr. (iii) (1·0 g.), b.p. 170—220°; and residue (1·5 g.). By i.r. spectroscopy fr. (ii) was a complex mixture with functional groups CO, $CONH_2$, CONH, OH and ether; fr. (iii) had caprolactam as a major component (80% by g.l.c.), but contained constituents with $CONH_2$ and CONH-groups.

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