

Reactions of Organic Peroxides. Part XVIII.¹ Photo-oxidation of Cyclohexylamine and Dicyclohexylamine

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Photo-oxidation of cyclohexylamine in various solvents gave products which included *N*-cyclohexyl-1-hydroperoxycyclohexylamine, cyclohexylamine-hydrogen peroxide adduct, *N*-cyclohexylidenecyclohexylamine, cyclohexanone oxime, 2'-cyclohexylcyclohexanespiro-3'-oxaziridine, amides, and 1-hydroperoxycyclohexylamine; dicyclohexylamine, under similar conditions, generally provided its hydrogen peroxide adduct in addition to *N*-cyclohexyl-1-hydroperoxycyclohexylamine and *N*-cyclohexylidenecyclohexylamine. Suggested routes to these products, based on results of control experiments, are given.

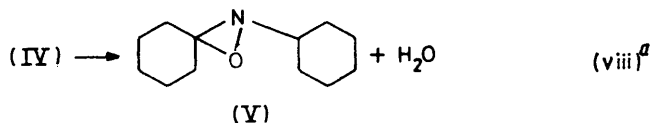
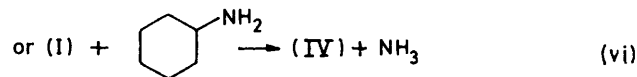
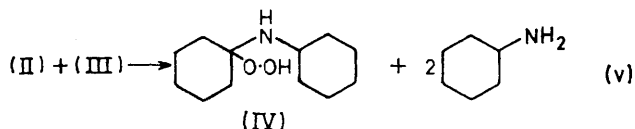
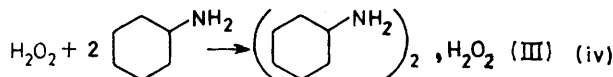
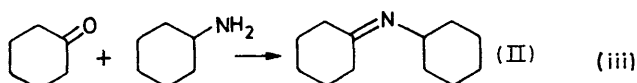
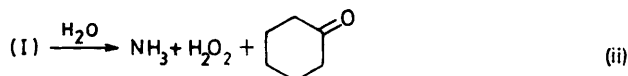
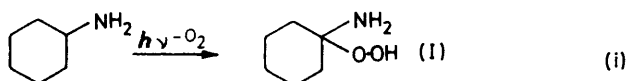
LITTLE information on the photosensitised oxidation of amines had appeared since the work of Schenck² until recently.^{3,4} Schenck indicated that the initial products of the oxygenation were hydroperoxy-amines, and the later work showed that the final products included carbonyl compounds, imines, and amides, some of these being derived from a multistage process.³

In the present work cyclohexylamine was photo-oxidised in various solvents and over the temperature range -20 to $+20^\circ$. Prolonged reaction (20–30 h) led to complex mixtures including *NN'*-dicyclohexyladipamide, 2'-cyclohexylcyclohexanespiro-3'-oxaziridine, and possibly *N*-cyclohexylhexenamide; some of these undoubtedly arise from autoxidation of *N*-cyclohexylidenecyclohexylamine.⁵ With shorter times of reaction (0.25–2.5 h), the nature of the products depended upon the solvent and temperature used; some of these (*N*-cyclohexyl-1-hydroperoxycyclohexylamine, cyclohexylamine-hydrogen peroxide adduct, and, occasionally, 1-hydroperoxycyclohexylamine) settled out as solids whilst others (the oxaziridine, *N*-cyclohexylidenecyclohexylamine, and cyclohexanone oxime) were isolated from the solutions. Ammonia was liberated during the oxidations.

Control experiments in the absence of oxygen and u.v. radiation showed that cyclohexylamine and 1-hydroperoxycyclohexylamine⁶ reacted together, with liberation of ammonia, to produce *N*-cyclohexylidenecyclohexylamine and either the amine-hydrogen peroxide adduct or *N*-cyclohexyl-1-hydroperoxycyclohexylamine.⁷ This reaction occurred most rapidly in polar solvents (*e.g.* alcohols) and when the ammonia was removed in a stream of nitrogen or by suction; in some cases high conversions (*ca.* 90%) into the hydroperoxy-amine were achieved.

The results are in accord with Scheme 1, in which only the first step requires photo-initiation. Whether reaction of cyclohexylamine with 1-hydroperoxycyclohexylamine (I) gave the adduct (III) or *N*-cyclohexyl-1-hydroperoxycyclohexylamine (IV) depended on the ratio of the reactants; a high ratio (*ca.* 6:1) of amine to hydroperoxide (I) generally afforded (III) whereas

lower ratios ($<4:1$) gave high yields of (IV). Equations (v), (vi), and (vii) represent alternative routes to (IV), but it was found that adduct (III) and imine (II) gave lower yields of (IV) than did the other routes.



^a Cf. ref. 7.

SCHEME 1

The nature of the products isolated depended to a considerable extent on their stability under the reaction

¹ Part XVII, E. G. E. Hawkins, *J. Chem. Soc. (C)*, 1971, 1474.

² G. O. Schenck, *Angew. Chem.*, 1957, **69**, 579.

³ F. C. Schaefer and W. D. Zimmermann, *J. Org. Chem.*, 1970, **35**, 2165.

⁴ R. F. Bartholomew and R. S. Davidson, *Chem. Comm.*, 1970, 1174.

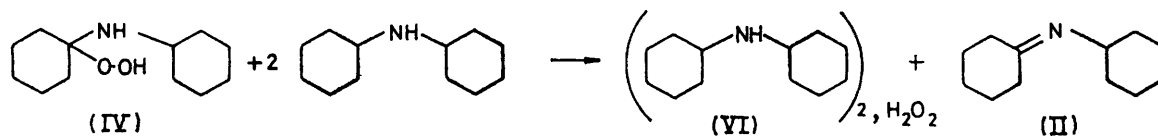
⁵ E. G. E. Hawkins, *J. Chem. Soc. (C)*, 1971, 160.

⁶ E. G. E. Hawkins, *J. Chem. Soc. (C)*, 1969, 2663.

⁷ (a) E. Höft and A. Rieche, *Angew. Chem.*, 1965, **77**, 548; (b) E. G. E. Hawkins, *J. Chem. Soc. (C)*, 1969, 2686.

conditions; *e.g.* the hydroperoxy-amine (IV) decomposed more rapidly in methanol than in isopropyl alcohol, particularly in the presence of ammonia, although this decomposition was considerably reduced by addition of a peroxide stabiliser [*e.g.* ethylenediaminetetra-acetic acid (EDTA)]. Such a result is in agreement with equation (vii) being reversible; the free hydrogen peroxide, derived from solutions of (IV), is rapidly destroyed under basic conditions (*e.g.* a large excess of ammonia). Further, loss of (IV) was rapid when solutions were photolysed in a quartz tube whereas a high proportion could be recovered when a Pyrex tube was used. The hydroperoxy-amine (IV) was isolated in yields of up to 50% (based on total active oxygen) from photo-oxidation in isopropyl alcohol-petroleum, and moderate yields were obtained on evaporation (at 20°) of the petroleum from a two-phase petroleum-water system.

Prolonged photo-oxidation of dicyclohexylamine gave mainly secondary amides (*e.g.* *NN'*-dicyclohexyladipamide) and acids (*e.g.* adipic acid), derived from autoxidation of the imine (II), produced by loss of hydrogen peroxide from the initially formed hydroperoxy-amine (IV). Reactions of shorter duration afforded low yields of (IV), the major product being generally the dicyclohexylamine-hydrogen peroxide adduct (VI). Control experiments showed that addition of an excess of dicyclohexylamine to (IV) gave the adduct (VI) and the imine (II), so that presumably the isolation of (VI) rather than (IV) from the photo-oxidations reflects the lower solubility of the adduct (VI) in the solvents used.



SCHEME 2

The other identified products from dicyclohexylamine included the imine (II) and, in lower yields, the oxaziridine (V).

EXPERIMENTAL

The photo-oxidations were carried out in a Hanovia photochemical reactor (both Pyrex and quartz) with a mercury-vapour lamp; oxygen was introduced through a sintered disc at the base of the tube containing the amine solution. The solution was cooled either by tap-water or by isopropyl alcohol pumped from a refrigerated system at -20 to 0°. The solutions contained benzophenone or Rose Bengal as photosensitiser.

Photo-oxidation of Cyclohexylamine.—(a) The amine (20 g) in petroleum (b.p. 60–80°; 120 ml) containing benzophenone (0.5 g) was irradiated through quartz at 20° for 2 h. On cooling, the solution provided *N*-cyclohexyl-1-hydroperoxycyclohexylamine (11.8 g), m.p. and mixed m.p. 87–88°. The filtrate was distilled to give fractions: (i) (1.75 g), b.p. 32° at 13 mmHg; (ii) (0.3 g), b.p. <70° at 13 mmHg; (iii) (0.55 g), b.p. 70–80° at 0.4 mmHg;

(iv) (1.4 g), b.p. 80–90° at 0.4 mmHg; and (v) residue (1.2 g). I.r. and mass spectroscopic analysis showed these fractions to contain cyclohexylamine (i), *N*-cyclohexylidenecyclohexylamine [ν_{\max} 6.02 μ m (C=N), *m/e* 179 (*M*), 164 (*M* - CH₃), 150 (*M* - C₂H₅), and 136 (*M* - C₃H₇)] (ii)–(iv), nitrocyclohexane [ν_{\max} 6.45 μ m] (ii), and cyclohexanone oxime [ν_{\max} 11.17 μ m, *m/e* 113 (*M*)] (iii) and (iv).

(b) The amine (20 g) in sodium-dried light petroleum (b.p. 60–80°; 120 ml) was oxidised as before for 20 min. The solid adduct (2.3 g) which precipitated had m.p. and mixed m.p. 54–56° after being washed with petroleum (Found: active oxygen equiv. 240; amine equiv. 118. Calc. for C₁₂H₂₆N₂.H₂O₂: active oxygen equiv. 232; amine equiv. 116). Cooling the filtrate provided *N*-cyclohexyl-1-hydroperoxycyclohexylamine (0.9 g).

(c) The amine (20 g) in petroleum (b.p. 40–60°; 110 ml) and water (10 ml) containing benzophenone (0.3 g) and EDTA as its sodium salt was oxygenated at 20° for 1 h as before. The petroleum was removed under reduced pressure at <20°. The residual slurry, on trituration with petroleum, provided impure *N*-cyclohexyl-1-hydroperoxycyclohexylamine (4.1 g), m.p. 77–81°.

(d) The amine (20 g) in petroleum (b.p. 40–60°; 50 ml) and ethanol (70 ml) containing Rose Bengal was oxygenated for 22.5 h, and the product was distilled at 1.5 mmHg to give, in addition to unchanged cyclohexylamine, four fractions: (i) (3.4 g), b.p. 110–120°; (ii) (4.2 g), b.p. 120–200°; (iii) (3.6 g), b.p. 200–250°; and (iv) residue (4.5 g). Fraction (i), a mixture (i.r.) of secondary amides, was shown by mass spectroscopy to contain *N*-cyclohexylformamide [*m/e* 127 (*M*), 126 (*M* - H), 112 (*M* - CH₃), 84 (*M* - C₃H₇), and 46 (*M* - C₆H₉)], *N*-cyclohexylacetamide [*m/e* 141 (*M*), 98 (*M* - CH₃), and 60 (*M* - C₆H₉)], dicyclohexylamine [*m/e* 181 (*M*) and 138 (*M* -

C₃H₇)], a compound C₁₂H₂₁NO (possibly an *N*-cyclohexylhexenamide), and an unidentified component, *m/e* 234 (C₁₆H₂₆N₂). From fraction (ii) was isolated a small amount of a solid, m.p. 279–280° (from ethanol), which had *m/e* 252 [C₁₄H₂₄N₂O₂, possibly *NN'*-dicyclohexyloxamide; fragment ions *m/e* 224 (*M* - CO), 171 (*M* - C₆H₉), and 126 (*M*/2)], and fraction (iii) yielded a solid, m.p. 242–245° (from ethanol), identified (mixed m.p.) as *NN'*-dicyclohexyladipamide.

The results of further photo-oxidations are summarised in the Table.

Photo-oxidation of Dicyclohexylamine.—(i) The amine (20 g) in benzene (90 ml) and methanol (13 ml) containing benzophenone (0.5 g) and EDTA (sodium salt; 0.3 g), was oxygenated in the Pyrex system at 20° for 5 h; the solution then contained 0.028 mol. equiv. of active oxygen. Solvent was removed under reduced pressure and the residue gave the dicyclohexylamine-hydrogen peroxide adduct (4.0 g), m.p. 89–91° (decomp.) (from ether) (Found: C, 71.7; H, 12.15; N, 6.8%; peroxide equiv. 375. Calc. for C₂₄H₄₆N₂.H₂O₂: C, 72.7; H, 12.1; N, 7.05%; peroxide

equiv. 396; amine equiv. 198), identical (mixed m.p.) with synthetic material [from amine and hydrogen peroxide in ether; m.p. 92–93° (Found: peroxide equiv. 390; amine equiv. 198)].

Distillation of the filtrate gave fractions shown by i.r. spectroscopy to consist largely of cyclohexanone, cyclohexylamine, and *N*-cyclohexylidenecyclohexylamine.

(ii) In three experiments different concentrations of amine in petroleum (b.p. 40–60°) were photo-oxidised

benzene with moisture excluded. Ammonia was evolved and after 0.5 h solid appeared (1.2 g), m.p. 54–55° (peroxide equiv. 230; amine equiv. 118), which was identical with the synthetic adduct (III). In the absence of a solvent, adduct (III) (3.75 g) was again produced after 2.5 h.

(ii) Hydroperoxy-amine (I) (10 g) and cyclohexylamine (20 g) were mixed and left at 20° overnight; ammonia was produced. Dilution with petroleum precipitated *N*-cyclohexyl-1-hydroperoxycyclohexylamine (3.4 g), m.p.

Photo-oxidation of cyclohexylamine

Amine (mol)	Solvent vol. (ml)	System used ^a	Temp.	Time (h)	Product		Remarks
					Active oxygen (mol)	Compounds identified	
0.2	MeOH (120)	Q	<i>b</i>	4	0.06		EDTA present
0.2	EtOH (120)	Q	<i>b</i>	3	0.018	Oxime (<1 g)	Phosphotungstic acid (2 g) present
0.2	Petroleum (60–80°) (120)	Q	<i>b</i>	{ 1 5.5	0.035 0.0195	(I), (IV), (V), oxime	
0.2	Petroleum (60–80°) (120)	Q	<i>b</i>	0.5		(III) (2.3 g) (IV) (0.9 g)	Carefully dried amine and solvent
0.06	Petroleum (40–60°) (140)	Q	<i>c</i>	2	0.015	Oxime (II)	
0.2	Ethanol (120)	Q	<i>b</i>	2	0.057		
0.2	{ Petroleum (40–60°) (100) Water (20)	Q	<i>b</i>	1	0.04	(IV) (1.2 g)	Rapid oxygen flow
0.2	MeOH (120)	Q	{ <i>c</i> <i>b</i>	2.75 2	0.041 0.0563		
0.2	MeOH (120)	P	<i>b</i>	4.5	0.0355	<i>e</i>	EDTA present
0.2	Pr ⁱ OH (120)	P	<i>b</i>	4	0.0475		EDTA present
0.2	Bu ⁱ OH (120)	P	<i>b</i>	4	0.0246	(III), (IV)	EDTA present
0.15	{ Pr ⁱ OH (80) DMF (40) ^d	P	<i>b</i>	4	0.0428		EDTA present
0.15	{ Pr ⁱ OH (110) MeNO ₂ (3)	P	<i>b</i>	4.5	0.056		EDTA present
0.12	{ Petroleum (105) Pr ⁱ OH (5)	P	<i>b</i>	1.5	0.031	(IV)	EDTA present
0.15	{ Petroleum (40–60°) (90) Pr ⁱ OH (25)	P	<i>b</i>	1	0.023	(III) (1.3 g) (IV) (2.33 g)	EDTA present
0.17	{ Petroleum (60–80°) (100) Pr ⁱ OH (20)	P	<i>b</i>	3.25	0.0345	(III) (<2.5 g) (IV) (2.8 g)	EDTA present
0.2	{ Petroleum (60–80°) (91) MeOH (13)	P	<i>b</i>	4.5	0.053		EDTA present
0.2	Pyridine (110)	P	<i>c</i>	5	0.0378	(III), oxime, (IV) (<3.7 g)	
0.2	Pyridine (110)	P	<i>c</i>	5.5	0.0214	(III), (IV), oxime	EDTA present

^a Q = Quartz; P = pyrex. ^b Flowing tap water in cooling jacket. ^c Cooled PrⁱOH in jacket, with inlet temp. –15 to –20° and outlet temp. –5 to +5°. ^d DMF = dimethylformamide. ^e Product distilled: fractions contained cyclohexylamine, cyclohexanone oxime, nitrocyclohexane, *N*-cyclohexylformamide, *N*-cyclohexylacetamide, *N*-cyclohexylhexanamide, octahydroacridine, and C₁₈H₂₁N (probably phenyloctahydroacridine).

at –20 to 0° for 1 h. A 4.2% solution provided the amine–hydrogen peroxide adduct but *N*-cyclohexyl-1-hydroperoxycyclohexylamine was isolated from 2.5 and 1% solutions.

(iii) The amine (20 g), in ethanol (120 ml) containing Rose Bengal, was photo-oxidised at 20° for 67.5 h; the final product contained 0.026 mol. equiv. of active oxygen of which 25% was lost on washing with water. *NN*-Dicyclohexyladipamide (0.3 g), m.p. and mixed m.p. 230–234°, crystallised from the solvent-free residue, which, on distillation, provided fractions containing (i.r. spectroscopy) cyclohexanone, cyclohexylamine, adipic acid, and secondary amides.

From a number of other experiments in benzene, pyridine, ethyl acetate, and benzene–methanol at 20° and at <0°, the dicyclohexylamine–hydrogen peroxide adduct was the major product isolated in each case.

Reaction of 1-Hydroperoxycyclohexylamine with Cyclohexylamine.—(i) The hydroperoxy-amine (I) (3 g) and cyclohexylamine (18 g) were stirred together at 20° in dry

87° (peroxide equiv. 217, amine equiv. 208). The filtrate, on distillation, provided fractions shown (by i.r. and mass spectroscopy) to contain cyclohexylamine, cyclohexanone, *N*-cyclohexylidenecyclohexylamine, and *N*-cyclohexylhexanamide (trace).

(iii) A solution of hydroperoxy-amine (I) (4.8 g) and cyclohexylamine (10 g) in methanol (130 ml) containing EDTA (0.2 g) was irradiated through Pyrex at 20° for 4 h in a stream of nitrogen. The loss of active oxygen was ca. 5%, and removal of the solvent at 20° left a residue (14.0 g) from which *N*-cyclohexyl-1-hydroperoxycyclohexylamine (4.4 g) was isolated. When the experiment was repeated in the quartz reactor only 10% of the active oxygen remained after 2.5 h.

In other experiments, carried out between 0 and 20° in other solvents (including petroleum, water, *t*-butyl alcohol, isopropyl alcohol, methanol–nitromethane, methanol–dimethylformamide, and methanol–petroleum), often in a stream of nitrogen or under slight vacuum, the hydroperoxy-amine (IV) was isolated in yields of up to 90%.

Reaction of Cyclohexylamine-Hydrogen Peroxide Adduct with N-Cyclohexylidenecyclohexylamine.—Imine (II) (5 g) and the adduct (III) (5 g) were dissolved in ethanol (10 ml) whereupon a rapid reaction occurred. Solid (3.5 g), m.p. 82–83° (peroxide equiv. 214, amine equiv. 205), separated out and was identified as *N*-cyclohexyl-1-hydroperoxycyclohexylamine (IV). Repetition of this reaction in ether at 0° overnight gave only the unchanged adduct.

Stability of N-Cyclohexyl-1-hydroperoxycyclohexylamine (IV).—The hydroperoxy-amine (8 g) was dissolved in methanol (130 ml) and ammonia was passed into the solution at 20° for 1.5 h. Only *ca.* 10% of the active

oxygen then remained, and distillation of the solution gave fractions (4.2 g) consisting largely of *N*-cyclohexylidenecyclohexylamine. Similar treatment in the presence of EDTA (0.2 g) led to recovery of (IV) (7.7 g).

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