Reactions of Organic Peroxides. Part XVI.[1] Amino-peroxides from Autoxidation of Imines

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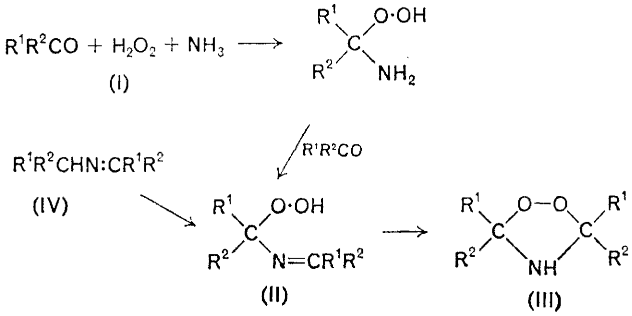
A number of imines $CH_2\cdot[CH_2]_4\cdot C{=}N\cdot CHR^1R^2$ (R^1 = aryl; R^2 = methyl or aryl), on oxygenation at −15 to −20° (u.v.) or at room temperature (R^1 and R^2 = aryl), gave the corresponding cyclic amino-peroxides $CH_2\cdot[CH_2]_4\cdot C\cdot NH\cdot CR^1R^2\cdot O\cdot O$. Thermal or base-catalysed decomposition of these amino-peroxides provided the corresponding ketones, R^1COR^2, caprolactam (low yield), and a number of by-products, some of which have been characterised. On the other hand the imines $Ph_2CH\cdot CH{:}NR$ ($R = C_6H_{11}$ or $CHPh_2$) gave rather unstable hydroperoxides, $Ph_2C(O\cdot OH)\cdot CH{:}NR$, on oxygenation.

SINCE it seems probable that the formation of cyclic amino-peroxides (III), from carbonyl compounds (I), hydrogen peroxide, and ammonia,[2] occurs *via* a hydroperoxy-imine (II), an alternative route to these peroxides (III), by autoxidation of the corresponding imines (IV), would appear to be possible.

However, our own work and that already described by other authors indicates that oxygen attack on imines occurs at the carbon side of the C=N system. Witkop[3] obtained fission products of the corresponding enamines by autoxidation of the imines (V) (R^1 = Ph; R^2 =



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[1] Part XV, E. G. E. Hawkins, *J. Chem. Soc.* (*C*), 1969, 2691.

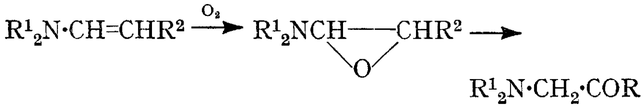
[2] E. G. E. Hawkins, *J. Chem. Soc.* (*C*), 1969, 2663, 2671, 2678.

[3] B. Witkop, *J. Amer. Chem. Soc.*, 1956, **78**, 2873.

Me or Ph), presumably *via* unstable hydroperoxides (VI):

$$\underset{\text{(V)}}{R^1R^2CH{\cdot}CH{=}N{\cdot}C_6H_4{\cdot}OMe\text{-}p} \longrightarrow \underset{\text{(VI)}}{R^1R^2C(O{\cdot}OH){\cdot}CH{=}N{\cdot}C_6H_4{\cdot}OMe\text{-}p} \longrightarrow R^1R^2CO + OHC{\cdot}NH{\cdot}C_6H_4{\cdot}OMe\text{-}p$$

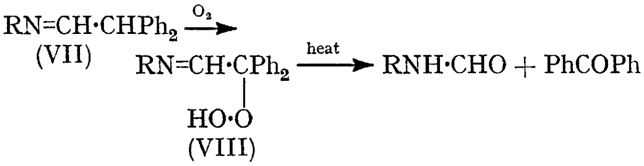
The autoxidation of Schiff bases of αβ-unsaturated ketones gave unsaturated diketones (after hydrolysis) probably *via* the corresponding enamines,[4] whereas some enamines autoxidise[5] to provide both double-bond cleavage products (as in photosensitised oxidation of enamines[6-8]) and α-amino-ketones, which could possibly arise from α-amino-epoxides:



$$R^1{}_2N{\cdot}CH{=}CHR^2 \xrightarrow{O_2} R^1{}_2NCH\underset{\diagdown O \diagup}{\text{——}}CHR^2 \longrightarrow R^1{}_2N{\cdot}CH_2{\cdot}COR$$

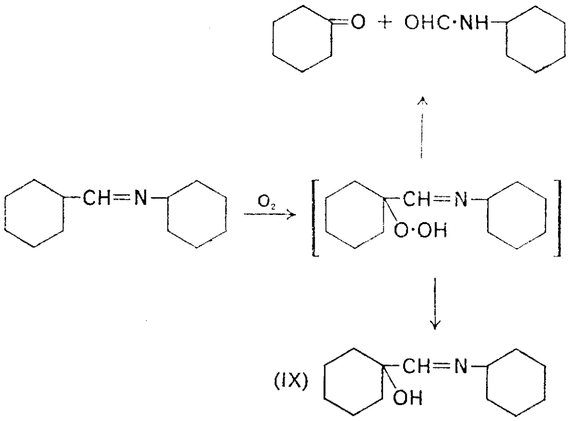
The reported production of secondary amides, BzNHAr, by photochemical oxygenation of imines PhCH=NAr[9] is rather surprising, since our own work has shown that imines (*e.g.* $C_6H_{11}N{:}CHPh$ or $C_6H_{11}N{:}CPh_2$) having neither a methylene (or methine) group α to the carbon of the C=N nor an *activated* methylene (or methine) group α to the nitrogen of the C=N were extremely unreactive to normal autoxidation conditions. However, the yields of these amides were low and the rates of oxidation slow; moreover, the best yields (10—11%) were obtained with isopropyl alcohol as solvent, raising the possibility that hydrogen peroxide—from photo-oxidation of the solvent—might be the actual oxidising agent, converting the imine into amide *via* α-hydroperoxy-amine[10] and oxaziridine (*cf.* ref. 11).

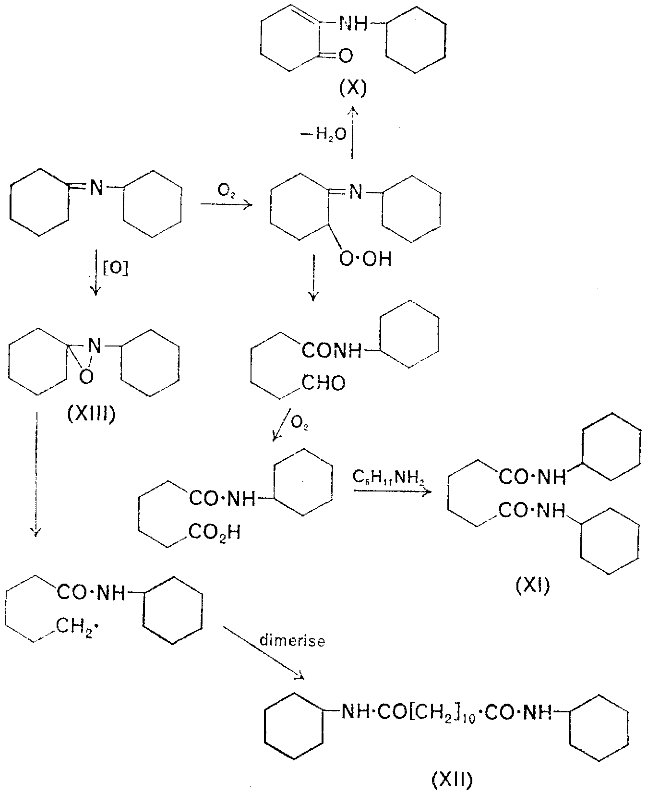
In the present work it has been confirmed that oxygen attack on an imine is normally at the α-position to the carbon of the C=N function; unstable, solid hydroperoxides (VIII) were obtained by low-temperature oxidation of (VII) ($R = C_6H_{11}$ and $R = Ph_2CH$):



$$\underset{\text{(VII)}}{RN{=}CH{\cdot}CHPh_2} \xrightarrow{O_2} \underset{\text{(VIII)}}{RN{=}CH{\cdot}\underset{\displaystyle HO{\cdot}O}{\underset{|}{C}}Ph_2} \xrightarrow{\text{heat}} RNH{\cdot}CHO + PhCOPh$$

and the products of autoxidation of *N*-hexahydrobenzylidenecyclohexylamine contained both *N*-cyclohexylformamide and a solid, m.p. 63—64°, with i.r., n.m.r., and mass spectra consistent with the α-hydroxy-imine (IX) derived from reduction of the initially-formed α-hydroperoxy-imine. *N*-Cyclohexylidenecyclohexylamine gave some of the aminocyclohexenone (X) on autoxidation but this was accompanied by varying amounts of *NN'*-dicyclohexyladipamide (XI), the *NN'*-dicyclohexyldiamide of 1,12-dodecanedioic acid (XII), and dark, polymeric material. These products could arise by the following routes shown in Scheme 1.





SCHEME 1

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[4] S. K. Malhotra, J. J. Hostynek, and A. F. Lundin, *J. Amer. Chem. Soc.*, 1968, **90**, 6565.

[5] R. A. Jerussi, *J. Org. Chem.*, 1969, **34**, 3648.

[6] C. S. Foote and J. W-P. Lin, *Tetrahedron Letters*, 1968, 3267.

[7] J. E. Huber, *Tetrahedron Letters*, 1968, 3271.

[8] K. Pfoertner and K. Bernauer, *Helv. Chim. Acta*, 1968, **51**, 1787.

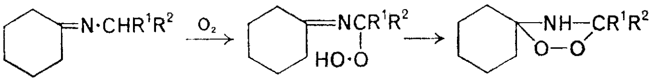
[9] Naoki Toshima and Hidefumi Hirai, *Tetrahedron Letters*, 1970, 433.

[10] E. Höft and A. Rieche, *Angew. Chem.*, 1965, **77**, 548.

[11] J-F. Dupin, *Bull. Soc. chim. France*, 1967, 3085.

From some experiments the oxaziridine (XIII) was identified in fractions of the chromatographed product. The diamide (XI) corresponds to the product, $C_{18}H_{20}N_2O_2$ (presumably *NN'*-diphenyladipamide), obtained by Witkop[3] from autoxidation of *N*-cyclohexylideneaniline.

However, when the methylene (or methine) group α to the nitrogen of the C=N function of the imines (XIV; R^1 = aryl) was activated by the introduction of aryl groups, autoxidation led to the formation of cyclic amino-peroxides (XV):

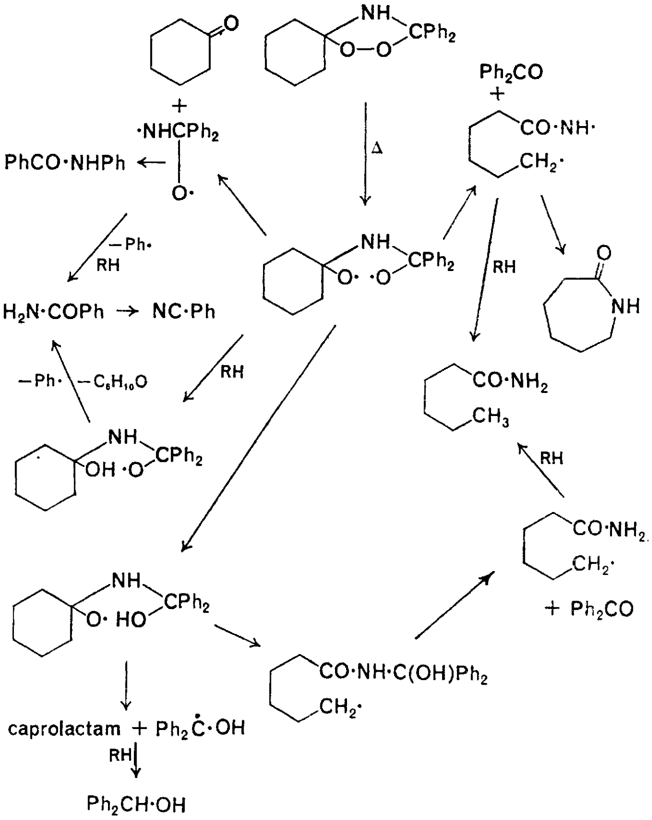


(XIV) (XV)

Oxygenation of solutions of (XIV) (R^2 = Me; R^1 = Ph, C_6H_4Cl-*p*, or $C_6H_4Me_2$-2,4), in light petroleum or benzene, at room temperature gave products with ⩽10% peroxides, but at −15 to −20° (u.v.) *ca.* 60—65% conversion to peroxides occurred, and the peroxides were purified by chromatography on silica gel. The imines (XIV) (R^1 = R^2 = Ph, C_6H_4Cl-*p*, or C_6H_4Me-*p*) under similar reaction conditions gave *ca.* 80% (at 20°) or 80—90% (at −15 to −20°) peroxides (XV), which crystallised after chromatography. *N*-Cyclohexylidenefluorenylamine (XIV; CH·R^1R^2 = fluorenyl), on the other hand, gave a peroxide-containing crude product which decomposed on silica gel and yielded chromatographic fractions consisting largely of fluorenone and *N*-fluorenylidenefluorenylamine. The imine (XIV; R^1 = Ph; R^2 = H) on oxidation at *ca.* −20° gave a product having *ca.* 60% peroxide, but this decomposed on chromatography on weakened silica gel. However, identification of cyclohexanone and benzamide in the products of thermal or base-catalysed decomposition of the crude peroxide was consistent with the presence of (XV; R^1 = Ph; R^2 = H) in the oxidate (*cf.* ref. 2).

The imine (IV; R^1 = R^2 = Ph) absorbed oxygen extremely slowly under the above conditions and a peroxide was not obtained, but oxygenation at 50°, with potassium t-butoxide in hexamethylphosphoramide, gave benzophenone and benzanilide, which could arise from the base-catalysed decomposition of the peroxide (III; R^1 = R^2 = Ph) in the same way as do cyclohexanone and caprolactam from 1,1'-peroxydicyclohexylamine.[2]

Thermal decomposition of (XV; R^1 = R^2 = Ph) gave a mixture of products; these included benzophenone (major product), cyclohexanone, caprolactam, diphenylmethane, tetraphenylethane, benzanilide, benzonitrile, caproamide, and possibly diphenylmethanol and diphenylmethylene(diphenylmethyl)amine. The formation of some of these products can be explained as in Scheme 2:



Scheme 2

There may be also loss of oxygen from the peroxide, regenerating the original imine, which, during the pyrolysis, might (i) provide $Ph_2CH\cdot$ radicals to yield diphenylmethane and tetraphenylethane, and (ii) undergo ketone exchange[12] with benzophenone to form the diphenylmethylene(diphenylmethyl)amine.

This amino-peroxide gave rather similar products to the above on photolysis, and, from the rather slow reaction with bases (*e.g.* sodium methoxide) or lithium chloride in methanol it afforded caprolactam (<30% theory), benzophenone (mainly), benzanilide, diphenylmethanol, cyclohexanone, and some of the minor products of pyrolysis. The use of sodium ethoxide in ethanol led to a considerable increase in diphenylmethanol production, at the expense of benzophenone, and to the formation of some methyloctahydroacridine; the parallel result from 1,1'-peroxydicyclohexylamine and sodium ethoxide[2] suggests that benzophenone is undergoing Ponndorf reduction with concomitant Oppenauer oxidation of ethanol to acetaldehyde, and the condensation product of this aldehyde with cyclohexanone leading to the acridine derivative. The mechanism for the production of caprolactam, benzophenone, cyclohexanone, and benzanilide is presumably similar to that for the base-catalysed decomposition of 1,1'-peroxydicyclohexylamine,[2] but with the difference that fission of a C–N link occurs in both possible directions.

The other amino-peroxides (XV; R^1 = Ar; R^2 = Me; and R^1 = R^2 = Ar) when heated with sodium meth-

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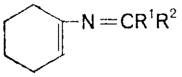
[12] A. Lawson and J. O. Stevens, *J. Chem. Soc.* (*C*), 1968, 1514.

oxide gave caprolactam (low yield), the corresponding ketones, R^1COR^2 (high yield), and small amounts of unidentified compounds, including substances thought (on mass spectroscopic evidence) to have structures of type (IV) and (XVI) (R^1 = Ar; R^2 = Me or Ar).



(XVI)

When heated with acids the peroxide (XV; R^1 = R^2 = Ph) was converted into cyclohexanone, benzophenone, and adipic acid or caprolactone.

EXPERIMENTAL

The imines were prepared by heating a solution of the required carbonyl compound with the amine in benzene under reflux, under a Dean–Stark head, until no further water was produced, followed by distillation or crystallisation of the product. The amines were either purchased or synthesised by the Leuckart Reaction[13] from the corresponding ketone and ammonium formate.

The oxygenation reactions were carried out, in light petroleum, benzene, or light petroleum–benzene solution, either (i) by stirring in oxygen, generally at room temperature, or (ii) in a Hanovia photochemical Pyrex reactor (mercury-vapour lamp) at −15 to −20° by pumping cooled isopropyl alcohol through the jacket of the reactor.

N-ββ-*Diphenylethylidenecyclohexylamine* (VII; R = C_6H_{11}).—This *imine*, m.p. 42—44° (from light petroleum) (Found: C, 86·6; H, 8·45; N, 4·95. $C_{20}H_{23}N$ requires C, 86·65; H, 8·3; N, 5·05%), had an n.m.r. spectrum at −20° [τ 2·47—2·67 (ArH, 10H), 3·18 (Ph_2CH, 1H), *ca.* 6·74 (N–C*H*, 1H), and 7·6—8·9 (ring CH_2, 10H)] consistent with the structure (VII; R = C_6H_{11}), but at room temperature, in $CDCl_3$, the spectrum [τ 2·4—2·85 (ArH, 10H), 3·30 (C*H*=C, 1H), 6·94 (N–C*H*, 1H), *ca.* 6·3 (N*H*, 1H), and 7·75—9·0 (ring CH_2, 10H)] was in agreement with that for the isomeric enamine, $C_6H_{11}NH{\cdot}CH{=}CPh_2$.

The imine (10 g.) in light petroleum (30 c.c.), was stirred in oxygen at 0—5° for 3½ hr.; 760 c.c. of oxygen was absorbed. Addition of further light petroleum and cooling provided crystalline N-(β-*hydroperoxy*-ββ-*diphenylethylidene*)*cyclohexylamine*, m.p. 44—48° (Found: C, 77·25; H, 7·9; N, 4·55%; peroxide equiv. = 332. $C_{20}H_{23}NO_2$ requires C, 77·65; H, 7·45; N, 4·55%; peroxide equiv. = 309); the peroxide decomposed fairly rapidly at room temperature so that accurate analytical figures were difficult to obtain. The n.m.r. spectrum of a fresh sample at −20° showed the expected proton environments for C_6H_5 (τ 2·53, 10H), N=C*H* (1·56, 1H), N–C*H* (6·72, 1H), and CH_2 (7·8—9·0, 10H), but at higher temperatures (−10°, 0°, 34·5°) the spectra of the decomposition products (Ph_2CO and $C_6H_{11}NHCHO$) became increasingly pronounced; the i.r. spectrum had weak OH and C=N (1658 cm⁻¹) absorption but could be reconciled to a structure $C_6H_{11}\overset{+}{N}H{=}CHC(OO^-)Ph_2$ (by proton transfer).

Reactions of the Hydroperoxy-imine (VIII; R = C_6H_{11}).—(a) *Thermal decomposition.* Decomposition of the hydroperoxide at 100—110° gave a product shown (by i.r. spectroscopy) to consist of a mixture of benzophenone and *N*-cyclohexylformamide.

(b) *With bases.* The hydroperoxide (7 g.) was stirred at 20° for 5 hr. with a solution of sodium (1 g.) in methanol (20 c.c.); a white solid (1·2 g.) was filtered off and the filtrate, on dilution with water and extraction with chloroform, followed by distillation of the chloroform extract, yielded fractions shown to consist of benzophenone and *N*-cyclohexylformamide. The solid, m.p. 96—99° (from methanol) (Found: C, 81·75; H, 7·8; N, 4·55. $C_{20}H_{23}NO$ requires C, 81·9; H, 7·85; N, 4·8%) had i.r. (C=N, OH), n.m.r. [τ *ca.* 2·82 (ArH, 10H), 6·78 (N–C*H*, 1H), 1·92 (N=C*H*, 1H), *ca.* 4·58 (O*H*, 1H), and 8·0—9·0 (ring CH_2, 10H)] and mass (*m/e* 293; $C_{20}H_{23}NO$) spectra consistent with the structure N-(β-*hydroxy*-ββ-*diphenylethylidene*)-*cyclohexylamine*.

This hydroxy-imine (0·5 g.), in addition to benzophenone and *N*-cyclohexylformamide, was also obtained by decomposition of the hydroperoxy-imine (4 g.) with triethylamine at 30—40°.

(c) *Reduction.* Addition of the hydroperoxy-imine (4·2 g.), in cooled ether, to a solution of triethyl phosphite (3 g.) in ether, initially at −15° and then at 20° overnight, followed by evaporation of the solvent and crystallisation of the residue from aqueous methanol, provided the same hydroxy-imine (3·6 g.), m.p. 96—98°, as in (b).

(d) *Hydrogenation.* A solution of the hydroperoxy-imine (5 g.) in ethanol (50 c.c.), containing 10% palladium on carbon (0·5 g.), was stirred in hydrogen (540 c.c. absorbed); the solution was filtered, the solvent evaporated, and the residue (3·5 g.) crystallised from light petroleum. The product (3·0 g.), m.p. 73—76° (Found: C, 81·05; H, 8·6; N, 4·6. $C_{20}H_{25}NO$ requires C, 81·35; H, 8·45; N, 4·75%), had i.r., n.m.r. [τ 2·1—2·8 (ArH, 10H), 6·54 (N–CH_2, 2H), 7·4 (N–C*H*, 1H), 6·90 (N*H* and O*H*, 2H), and 7·8—9·0 (ring CH_2, 10H)] and mass spectra consistent with it being N-(β-*hydroxy*-ββ-*diphenylethyl*)*cyclohexylamine*.

N-ββ-*Diphenylethylidenediphenylmethylamine* (VII; R = $CHPh_2$).—This imine, m.p. 89—92° (from ethanol), b.p. 235—250°/0·5 mm., also appeared to be in equilibrium with the corresponding enamine, $Ph_2CH{\cdot}NH{\cdot}CH{=}CPh_2$ (by n.m.r. spectrum), and it autoxidised extremely readily.

The imine (10 g.), in light petroleum (80 c.c.) and benzene (80 c.c.), was photo-oxidised at −20° for 2 hr.; solid (5·5 g.), which had separated, on recrystallisation from ethyl acetate–methanol, gave crops with peroxide equiv. = 410—430 (3·2 g.) and 595 (1·9 g.), but rapid decomposition of the peroxide occurred on further attempts at purification. A sample of N-(β-*hydroperoxy*-ββ-*diphenylethylidene*)*diphenylmethylamine*, m.p. 99—101° (from ethyl acetate) (Found: C, 82·15; H, 5·95; N, 3·3%; peroxide equiv. = 402. $C_{27}H_{23}NO_2$ requires C, 82·45; H, 5·85; N, 3·55%; peroxide equiv. = 393) was isolated by rapid crystallisation from cold solvent. The i.r. spectrum showed evidence for C=N and strong hydrogen bonding; no satisfactory n.m.r. spectrum could be obtained owing to decomposition.

On storage, solutions of the hydroperoxy-imine deposited *N*-formyl(diphenylmethyl)amine, m.p. 135—137° (from benzene), [*m/e* 211 ($C_{14}H_{13}NO$)], and the filtrates contained benzophenone.

N-*Diphenylmethylenediphenylmethylamine* (IV; R^1 = R^2 = Ph).—Solutions of the imine, m.p. 150—153° [lit.,[14]

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[13] M. L. Moore, *Org. Reactions*, 1949, **5**, 301.

[14] C. K. Ingold and C. L. Wilson, *J. Chem. Soc.*, 1933, 1493.

152°], in light petroleum–benzene, failed to absorb oxygen at 20° and at −20° (u.v.) gave only *ca.* 9% conversion into peroxide in 4 hr.

A solution of the imine (10·5 g.) in hexamethylphosphoramide (35 c.c.), containing potassium t-butoxide (from 2 g. potassium), was stirred in oxygen; it failed to react at room temperature but at 50° it absorbed oxygen (810 c.c.) in 3 hr. Benzanilide (3·0 g.), m.p. and mixed m.p., 164—167°, was filtered off and the filtrate, after dilution with water and extraction with ether, afforded distilled fractions (7·7 g.) shown (by i.r.) to contain benzophenone and further benzanilide.

N-*Cyclohexylidenediphenylmethylamine* (XIV; $R^1 = R^2 = Ph$).—(i) The imine (12 g.), m.p. 68—70°, in light petroleum (50 c.c.) and benzene (50 c.c.), was photo-oxidised at −15° for 2 hr. Evaporation of the solvent left a crude product (12·4 g.), peroxide equiv. = 325, which, by chromatography on silica gel (activity II), gave the *amino-peroxide* (XV; $R^1 = R^2 = Ph$), m.p. 48—50° (from light petroleum) (Found: C, 77·4; H, 7·35; N, 4·65%; peroxide equiv. = 287 (*a*), 305 (*b*). $C_{19}H_{21}NO_2$ requires C, 77·3; H, 7·1; N, 4·75%; peroxide equiv. = 295). The peroxide equiv. (*a*) was determined by heating the sample with solid sodium iodide, acetic acid, and concentrated hydrochloric acid for 20 min. and that (*b*) by heating the sample with saturated potassium iodide solution and acetic acid for 5 min., in both cases in the presence of solid sodium hydrogen carbonate. The i.r. (NH absorption), n.m.r. [τ 2·2—3·4 (ArH, 10H), 6·9 (N*H*, 1H), and 8·0—9·0 (ring CH_2, 10H)], and mass [*m*/*e* 295 ($C_{19}H_{21}NO_2$)] spectra were in agreement with the above structure.

The above photo-oxidation gave similar results in the presence of benzophenone, but, with added t-butylcatechol, the oxidation was inhibited, indicative that the reaction involved autoxidation (*i.e.* by radical chains) rather than photo-sensitised oxidation (*i.e.* by singlet oxygen).

(ii) The imine (10 g.), in benzene (15 c.c.) containing azobisisobutyronitrile (trace), was stirred in oxygen at 10° for 6 hr. and yielded crude peroxide (10·2 g.), peroxide equiv. = 326 (91% pure). Similar oxidations were carried out at 20° in benzene (2 hr.), ethyl acetate (3 hr.), and methanol (7 hr.) to give peroxide of 80—85% purity. Crystalline peroxide was obtained from these products by chromatography, as above.

Reactions of the Peroxy-amine (XV; $R^1 = R^2 = Ph$).—(a) *Pyrolysis*. (i) Peroxide (81% pure; 10 g.), dissolved in a mixture of light petroleum and ether, was decomposed by gradually dropping the solution into a flask at *ca.* 200°. Distillation of the final product at 18 mm. gave: fr. 1 (0·7 g.), b.p. 80—160°; fr. 2 (3·0 g.), b.p. 160—180°; fr. 3 (1·8 g.), b.p. 180—220°; fr. 4 (2·1 g.), b.p. 220—280°; and residue (1·4 g.). By i.r. spectroscopy, fr. 1 was mainly cyclohexanone, with *ca.* 10% benzophenone; fr. 2 was benzophenone with *ca.* 7% caprolactam; fr. 3 and fr. 4 also contained benzophenone and other components. Chromatography of fr. 3 and fr. 4 on silica gel gave fractions which contained benzophenone (mainly), diphenylmethane, 1,1,2,2-tetraphenylethane (m.p. 211—213°), and diphenylmethanol (trace).

(ii) Peroxide (pure; 10 g.), in benzene (10 c.c.), was fed into a heated tube containing glass beads, at 400° during 25 min., under nitrogen. Distillation of the product at 10 mm. gave fractions: (1) (6·1 g.), b.p. 120—140°; (2) (2·0 g.), b.p. 140—205°; and residue (0·4 g.). Analysis of the fractions by g.l.c. showed that fr. 1 contained benzophenone (68·2%), caprolactam (15·6%), diphenylmethane (9·8%), benzonitrile (6·3%), cyclohexanone (trace), caproamide (trace), and two unidentified peaks; fr. 2 had benzophenone (55·5%), caproamide (12·1%), benzonitrile (10·4%), and several unidentified compounds.

(b) *Photolysis*. Peroxide (pure; 10 g.), in light petroleum (50 c.c.) and benzene (50 c.c.), was photolysed in the quartz Hanovia reactor at *ca.* 20° in a slow stream of nitrogen for 14 hr. The distilled product provided fractions shown spectroscopically to consist largely of benzophenone, but containing caprolactam, diphenylmethane, the imine (IV; $R^1 = R^2 = Ph$), and compounds with *m*/*e* 261 [$C_{19}H_{19}N$, probably (XIV; $R^1 = R^2 = Ph$)], 257 [$C_{19}H_{15}N$, possibly $PhN{=}CPh_2$], 181 ($C_{13}H_{11}N$), and 180 ($C_{13}H_{10}N$).

(c) *With bases*. (i) Peroxide (84%; 10 g.) was heated at 100—110° (bath) for 4 hr. with a solution of sodium (2 g.) in methanol (40 c.c.); the decomposition product was diluted with water and extracted with chloroform. Distillation of the extract at 12 mm. gave: fr. 1 (4·0 g.), b.p. 140—162°; fr. 2 (1·9 g.), b.p. 162—170°; fr. 3 (1·2 g.), b.p. 170—220°; and residue (1·3 g.). By i.r. spectroscopy, fr. 1 was shown to contain benzophenone with *ca.* 10% caprolactam and fr. 2 was largely benzophenone. Fr. 3 crystallised to afford benzanilide (1·0 g.), m.p. and mixed m.p., 159—162°. The aqueous phase was acidified with hydrochloric acid and re-extracted with chloroform; the residue (1·0 g.) from this extract was shown (by mass spectroscopy) to contain benzophenone, caprolactam, benzoic acid, and a primary amide.

(ii) Peroxide (84%; 11 g.) was heated under reflux with a solution of sodium (2 g.) in ethanol (40 c.c.) for $\frac{3}{4}$ hr.; the peroxide decomposed and ammonia was produced. The cooled solution was acidified and extracted with chloroform; the residue from this extract, on distillation at 15 mm. gave: fr. 1 (2·5 g.), b.p. 140—168°; fr. 2 (3·0 g.), b.p. 168—210°; fr. 3 (1·2 g.) b.p. 210—240°; and residue (1·3 g.). By g.l.c. and i.r. spectroscopy, fr. 1 was shown to contain cyclohexanone (10·0%), caproamide (5·2%), caprolactam (10·3%), benzophenone (54·2%), and, diphenylmethanol (20·3%), and fr. 2 had caproamide (1·2%), caprolactam (5·7%), benzophenone (58·0%), diphenylmethanol (35·0%), and benzanilide (0·7%), with traces of benzonitrile and diphenylmethane. Fr. 3 contained benzophenone (*ca.* 40%), diphenylmethane, diphenylmethanol, methyloctahydroacridine, and an imine ($C_{19}H_{15}N$).

The peroxide was also decomposed by heating it with sodium hydroxide in methanol (12 hr.), lithium chloride in methanol (12 hr.), and sodium methoxide in acetonitrile ($1\frac{1}{2}$ hr.) and in dimethyl sulphoxide ($\frac{1}{4}$ hr.); the products were qualitatively the same as from (i).

(d) *With Acids*. The peroxide, heated with aqueous ethanol containing sulphuric acid, gave benzophenone, cyclohexanone, and a small amount of diethyl adipate; with formic acid it yielded caprolactone in place of the ester.

N-*Cyclohexylidene-di-*p*-tolylmethylamine* (XIV; $R^1 = R^2 = C_6H_4Me$-*p*).—(i) The imine (15 g.), m.p. 53—56°, in light petroleum (50 c.c.) and benzene (50 c.c.), was photo-oxidised at −15 to −20° (u.v.) for 3 hr., to give a crude product (15·7 g.), peroxide equiv. = 411 (80% pure). Chromatography on silica gel (activity V) gave crystalline *amino-peroxide* (XV; $R^1 = R^2 = C_6H_4Me$-*p*), m.p. 80—82° (Found: C, 77·9; H, 7·85; N, 4·05%; peroxide equiv.

= 339. $C_{21}H_{23}NO_2$ requires C, 78·0; H, 7·75; N, 4·35%; peroxide equiv. = 323); the i.r. and mass spectra were consistent with the proposed structure.

(ii) A solution of the imine (10 g.) in light petroleum (15 c.c.), containing azobisisobutyronitrile, stirred in oxygen at 20° for 6 hr. absorbed 680 c.c. Normal work-up gave the peroxide (6·8 g.) as above, m.p. 77—79°, peroxide equiv. = 341.

This peroxide, when heated with sodium methoxide in methanol (32 hr.), yielded *p,p′*-dimethylbenzophenone (85—90% theoretical), caprolactam (*ca.* 25% theoretical) and unidentified imines.

N-*Cyclohexylidene-bis-*(p-*chlorophenylmethyl*)*amine* (XIV; $R^1 = R^2 = C_6H_4Cl$-*p*).—(i) The imine (10 g.), m.p. 54—56°, in light petroleum (80 c.c.) and benzene (80 c.c.), photo-oxidised at −15 to −20° for 2½ hr., provided a product (9·0 g.), peroxide equiv. = 410, which, from ethyl acetate, afforded the *amino-peroxide* (5·5 g.) (XV; $R^1 = R^2 = C_6H_4Cl$-*p*), m.p. 125—127° (Found: C, 62·3; H, 5·2; Cl, 19·55; N, 3·7%; peroxide equiv. = 367. $C_{19}H_{19}Cl_2NO_2$ requires C, 62·65; H, 5·2; Cl, 19·5; N, 3·85%; peroxide equiv. = 364).

(ii) The imine (4 g.), in light petroleum (20 c.c.), was stirred in oxygen at 20° for >12 hr., but the conversion into peroxide was only *ca.* 20%; chromatography of the crude product on silica gel gave the above amino-peroxide (0·7 g.) and material (2·1 g.), b.p. 260—310°/10 mm., shown by mass spectroscopy to consist of a mixture of bis-(*p*-chlorophenyl)methane, bis-(*p*-chlorophenylmethyl)amine, *p,p′*-dichlorobenzophenone, (XIV; $R^1 = R^2 = C_6H_4Cl$-*p*, and (IV; $R^1 = R^2 = C_6H_4Cl$-*p*).

Decomposition of this peroxide with sodium methoxide (16 hr.) gave *p,p′*-dichlorobenzophenone (85—90% theoretical), caprolactam (trace), and unidentified material.

N-*Cyclohexylidenefluoren-9-ylamine* (XIV; CHR^1R^2 = fluorenyl).—(i) The imine (10 g.), m.p. 101—103° (Found: C, 87·1; H, 7·45; N, 5·25. $C_{19}H_{19}N$ requires C, 87·35; H, 7·3; N, 5·35%), suspended in a mixture of light petroleum (50 c.c.) and benzene (50 c.c.), was photo-oxidised at −10 to to −20° for 2 hr. Although the imine had dissolved the peroxide content of the solution did not increase after the first hour. Evaporation of the solvent left a residue (10·1 g.), peroxide equiv. = 1280 (*ca.* 23% conversion), but chromatography on silica gel (activity V) brought about decomposition of the peroxide and yielded a solid (1·5 g.), m.p. 171—173° (lit.,[14] 175°) (from methanol), *m/e* 343 ($C_{26}H_{17}N$; *N*-fluorenylidenefluorenylamine).

(ii) Autoxidation of a solution of the imine (7 g.) in benzene (15 c.c.) at 20° for 8 hr. led to absorption of 670 c.c. oxygen, and, on evaporation of solvent, a residue with peroxide equiv. = 608 (43% conversion). On addition of light petroleum this provided the above ($C_{26}H_{17}N$) imine (2·6 g.), m.p. 171—173°, and chromatography of the filtrate yielded only fluorenone and benzophenone.

N-*Cyclohexylidene-α-methylbenzylamine* (XIV; R^1 = Ph; R^2 = Me).—(i) The imine (15 g.), b.p. 149—152°/10 mm., in light petroleum (50 c.c.) and benzene (50 c.c.), photo-oxidised at −15° for 2 hr., gave, after removal of the solvent, a residue (15·7 g.), peroxide equiv. = 384. Repeated chromatography on silica gel (activity IV—V), using initially 1 : 1 benzene–light petroleum for development, then 1 : 3, 1 : 5, and finally pure light petroleum, afforded the *amino-peroxide* (9·4 g.) (XV; R^1 = Ph; R^2 = Me) (Found: peroxide equiv. = 246. $C_{14}H_{19}NO_2$ requires peroxide equiv. = 233), which partially decomposed on attempted distillation at 0·3 mm.

(ii) The neat imine (15 g.), stirred in oxygen at 20° for 4 hr., absorbed 670 c.c. oxygen (38% theoretical), but the product had a peroxide equiv. = 2170 (*ca.* 10% on imine). Imine (15 g.), in light petroleum (25 c.c.) containing azobisisobutyronitrile, absorbed oxygen (910 c.c.) in 6 hr. at 20°, but the solvent-free residue contained only a trace of active oxygen, and by i.r. and mass spectroscopy was shown to contain cyclohexanone, acetophenone, (XIV; R^1 = Ph; R^2 = Me), (IV; R^1 = Ph; R^2 = Me), a compound $C_{14}H_{15}N$ (possibly PhNH·CHPhMe), and a compound $C_{20}H_{27}N$.

Reactions of the Peroxy-amine (XV; R^1 = Ph; R^2 = Me).—(a) *With Sodium Methoxide.* The peroxide (9 g.) was heated under reflux with a solution of sodium (2 g.) in methanol (40 c.c.) for 4 hr. Normal work-up gave, on distillation at 10 mm.: fr. 1 (2·8 g.), b.p. 48—80°; fr. 2 (3·5 g.), b.p. 80—165°; fr. 3 (1·0 g.), b.p. 165—230°; and residue (0·5 g.). Analysis of these fractions by i.r. and mass spectroscopy showed that fr. 1 contained mainly acetophenone, with *ca.* 10% cyclohexanone; fr. 2 had acetophenone, caprolactam (10—15%), (IV; R^1 = Ph; R^2 = Me), a compound $C_{14}H_{17}N$ [probably (XVI; R^1 = Ph, R^2 = Me)], and ions corresponding to traces of $C_{16}H_{17}N$ and $C_{15}H_{15}N$.

(b) *With Lithium Chloride in Methanol.* The peroxide (16 g.) was heated under reflux with a solution of lithium chloride (10 g.) in methanol (40 c.c.) for 4 hr., to give again a mixture of cyclohexanone, acetophenone, caprolactam, and imines.

N-*Cyclohexylidene-*p-*chloro-α-methylbenzylamine* (XIV; $R^1 = C_6H_4Cl$-*p*; R^2 = Me).—(i) The imine (15 g.), b.p. 174—178°/15 mm. (Found: C, 71·0; H, 7·6; Cl, 14·55; N, 5·5. $C_{14}H_{18}ClN$ requires C, 71·35; H, 7·65; Cl, 15·05; N, 5·95%), on photo-oxidation for 3 hr. (as above) gave a crude product containing *ca.* 60% peroxide; repeated chromatography on silica gel afforded the *amino-peroxide* (5·2 g.) (XV; $R^1 = C_6H_4Cl$-*p*; R^2 = Me), *ca.* 93% pure (Found: peroxide equiv. = 287·5. $C_{14}H_{18}ClNO_2$ requires peroxide equiv. = 267·5). The i.r. and mass [*m/e* 267 ($C_{14}H_{18}ClNO_2$), 251 (*M* − O), 249 (*M* − H_2O), 234 (*M* − HO_2), 170 (C_8H_9ClNO)] spectra were consistent with the structure, and the impurities included *p*-chloroacetophenone and imine.

(ii) The imine (15 g.), in light petroleum (25 c.c.) containing azobisisobutyronitrile, absorbed oxygen (705 c.c.; 48% theoretical) in 2 hr. at room temperature, but the product contained only 12·5% peroxide (based on active oxygen). Distillation of the product gave fractions shown (by i.r. and mass spectroscopy) to contain cyclohexanone, *p*-chloroacetophenone, *p*-chloro-α-methylbenzylamine, and the imine.

The product from the reaction of the peroxide (5 g.) with sodium (1 g.) in methanol (20 c.c.) (refluxed, 3 hr.), on distillation at 10 mm. gave: fr. 1 (1·8 g.), b.p. 120—135°; fr. 2 (0·8 g.), b.p. 135—185°; fr. 3 (0·9 g.), b.p. 185—240°; and residue (0·5 g.). From the i.r. and mass spectra, fr. 1 was shown to consist largely of *p*-chloroacetophenone; fr. 2 was also mainly this ketone, with *ca.* 20% caprolactam and a trace of a compound *m/e* 183 ($C_9H_{10}ClNO$); fr. 3 contained 10—12% caprolactam, the ketone, a compound *m/e* 386 [$C_{22}H_{24}Cl_2N_2$, possibly (XVII; Ar = *p*-ClC_6H_4)], and unidentified substances.

$$\mathrm{ArMeCH{\cdot}N{:}\overline{C{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}C}{\cdot}NH{\cdot}CHMeAr}$$

(XVII)

N-*Cyclohexylidene*-α,2,4-*trimethylbenzylamine* (XIV; $R^1 = C_6H_3Me_2$-2,4; R^2 = Me).—(i) Imine (15 g.), b.p. 170—174°/15 mm. [*m/e* 229 ($C_{16}H_{23}N$)], on photo-oxidation (as above) yielded a peroxide-containing product (66%), and repeated chromatographic treatment gave the *amino-peroxide* (6·0 g.) (XV; $R^1 = C_6H_3Me_2$-2,4; R^2 = Me), *ca.* 94% pure (Found: peroxide equiv. = 277. $C_{16}H_{23}NO_2$ requires peroxide equiv. = 261). The i.r. and mass [*m/e* 261 ($C_{16}H_{23}NO_2$), 228 ($M - HO_2$), 164 ($C_{10}H_{14}NO$)] spectra were in agreement with this formulation; the impurities consisted of 2,4-dimethylacetophenone and the imine.

(ii) Autoxidation of the imine in light petroleum at room temperature (as above) led to absorption of 42% of the theoretical amount of oxygen, but again the peroxide content (*ca.* 7·5%) was low. The distilled products from this reaction were found to contain cyclohexanone, 2,4-dimethylacetophenone, the starting imine, the imine (IV; $R^1 = C_6H_3Me_2$-2,4; R^2 = Me), and a compound *m/e* 374 [$C_{26}H_{34}N_2$, possibly (XVII; Ar = $C_6H_3Me_2$-2,4)].

Treatment of this peroxide with sodium methoxide, as before, yielded a product containing 2,4-dimethylacetophenone, compounds with *m/e* 227 [$C_{16}H_{21}N$, probably (XVI; $R^1 = C_6H_3Me_2$-2,4; R^2 = Me)] and 251 ($C_{18}H_{21}N$), as well as unidentified substances.

N-*Cyclohexylidenebenzylamine* (XIV; R^1 = Ph; R^2 = H).—(i) Photo-oxidation, at −20°, of a solution of the imine (20 g.), b.p. 162—165°/10 mm., in light petroleum (75 c.c.) and benzene (75 c.c.), for 6 hr. followed by removal of the solvent, provided a residue (21·1 g.), peroxide equiv. = 371 (59% conversion). Attempts to concentrate the peroxide by chromatography on silica gel resulted in almost complete loss of active oxygen.

(ii) A similar photo-oxidation of the imine (10 g.) gave a product (10·6 g.), peroxide equiv. = 690, which was heated with triethylamine (25 c.c.) for 10 min. to decompose the peroxide. Distillation of the product at 10 mm. gave: fr. 1 (0·1 g.), b.p. <65°; fr. 2 (1·1 g.), b.p. 165—172°; fr. 3 (1·3 g.), b.p. 172—215°; fr. 4 (2·0 g.), b.p. 215—315°; fr. 5 (2·1 g.) b.p. 280—295°/0·2 mm.; and residue (3·0 g.). By spectroscopic examination fr. 1 was shown to contain cyclohexanone; fr. 2 and fr. 4 consist mainly of benzamide, but groups CONH, CO_2H, and C≡N were also present; and fr. 5 contained unidentified secondary amides and a compound *m/e* 263 ($C_{19}H_{21}N$, possibly 1,2,3,4,5,6,7,8-octahydro-9-phenylacridine).

N-*Cyclohexylidenecyclohexylamine*.—(i) The imine (20 g.), b.p. 125—126°/15 mm., in light petroleum (b.p. 60—80°; 80 c.c.) was oxygenated at 0° for 4¾ hr. in a flask fitted with a recycle stirrer; 1·8 l. of oxygen were absorbed. The light petroleum solution was decanted from the semisolid sludge; the latter, on trituration with acetone, afforded a solid (2·2 g.), m.p. 238—242° (from ethanol), undepressed on admixture with synthetic *NN′*-dicyclohexyladipamide. The decanted light petroleum and mother liquors were combined, the solvent was evaporated, and the residue was chromatographed on alumina. The early fractions (8·3 g.) were shown, by i.r. spectroscopy, to consist of a mixture of cyclohexanone and *N*-cyclohexyl-2-aminocyclohex-2-enone (X) (see below); the following eluates (6·5 g.), triturated with acetone, provided further *NN′*-dicyclohexyladipamide; and the final fractions (2·1 g.) also consisted largely of secondary amides and from these was isolated *NN′*-dicyclohexyl-1,10-dicarbamoyldecane, m.p. 189—191° (from ethanol), undepressed on admixture with the synthetic diamide.

The oxo-enamine (X), b.p. 160°/14 mm., was separated from the cyclohexanone by distillation; the i.r. spectrum showed absorption due to secondary amine (3400 cm.$^{-1}$) and αβ-unsaturated carbonyl (1678 cm.$^{-1}$) groups, and n.m.r. spectrum C=C*H* (τ 4·76, 1H), N*H* (5·97, 1H), N–C*H* (7·13, 1H) and C*H*$_2$–C= and C*H*$_2$–C=O (7·4—7·85, 4H). The structure was confirmed (*a*) by heating the compound with a solution of 2,4-dinitrophenylhydrazine in hydrochloric acid to provide the bis-2,4-dinitrophenylhydrazone of cyclohexane-1,2-dione, m.p. and mixed m.p. 234—236°, and (from the filtrate) cyclohexylamine hydrochloride, and (*b*) by synthesis, in low yield, from reaction of cyclohexylamine with cyclohexane-1,2-dione.

(ii) Oxygenation of the imine (20 g.) in ethanol (50 c.c.), with suspended, dried magnesium sulphate (7 g.), as in (i) was carried out at 65° (8½ hr.), then 80° (9 hr.); 1 l. of oxygen was absorbed. Chromatography of the filtered, solvent-free product gave fractions (8·2 g.) containing cyclohexanone (minor amount), compound (X) and 2-cyclohexyl-3-pentamethyleneoxaziridine (XIII), and later fractions (3·0 g.; 1·2 g.; 3·8 g.) shown (by i.r.) to consist mainly of secondary amides, similar to those from run (i).

N-*Hexahydrobenzylidenecyclohexylamine*.—The imine (25 g.), b.p. 126—128°/15 mm., was stirred (neat) in oxygen at 48° for 5 hr.; oxygen (815 c.c.) was absorbed and part of the product (active oxygen equiv. = 1017) was chromatographed on silica gel. The fractions, by i.r. and mass spectroscopy, were shown to contain compounds $C_{13}H_{23}NO$ (possibly $C_6H_{11}CONHC_6H_{11}$), $C_{20}H_{33}NO_2$ [possibly $C_6H_{11}N(COC_6H_{11})_2$], $C_7H_{13}NO$ (*N*-cyclohexylformamide), and a second compound $C_{13}H_{23}NO$ having C=N and OH absorption (see below).

Distillation of part of the above oxidate gave starting material (*ca.* 60%), a fraction (*ca.* 10%), b.p. 140—160°/15 mm., and higher-boiling fractions containing secondary amides. Crystallisation of the middle fraction, from light petroleum, gave the *hydroxy-imine* (IX), m.p. 63—64°, with i.r. (C=N, 1658 cm.$^{-1}$, and OH, 3330 cm.$^{-1}$), n.m.r. [τ 2·36 (N=C*H*, 1H), 6·94 (N–C*H*, 1H), 5·94 (O*H*, 1H), and 7·9—8·9 (ring C*H*$_2$, 20H)] and mass [*m/e* 209 ($C_{13}H_{23}NO$)] spectra consistent with this formulation.

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