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Reactions of Organic Peroxides. Part XIII [1] Amino-peroxides from Carbonyl Compounds, Ammonia, and Hydroperoxides

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Reaction of cyclohexanone with t-butyl hydroperoxide and ammonia gave 1-t-butylperoxycyclohexylamine which formed normal amine derivatives with phenyl isocyanate, acetyl chloride, benzoyl chloride, ethyl chloroformate, t-butyl hypochlorite, and toluene-*p*-sulphonyl chloride. Decomposition of the peroxyamine and several of its derivatives by pyrolysis and by treatment with bases was studied. When t-butyl hydroperoxide was replaced by cumene hydroperoxide the product contained the corresponding 1-cumylperoxycyclohexylamine. Treatment of acyclic ketones with t-butyl hydroperoxide and ammonia gave no peroxyamines, whereas evidence was obtained that acyclic aldehydes (acetaldehyde and n-butyraldehyde) gave rise to diperoxyamines.

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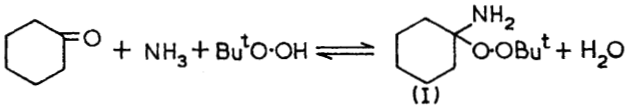
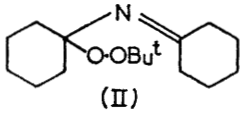
THE formation of 1,1′-peroxy-amines and 1-hydroperoxy-amines from carbonyl compounds, hydrogen peroxide, and ammonia, has been described in preceding papers. When cyclohexanone was treated with ammonia and t-butyl hydroperoxide an equilibrium mixture was formed which contained t-butylperoxycyclohexylamine (I). Extraction and distillation of this peroxy-amine



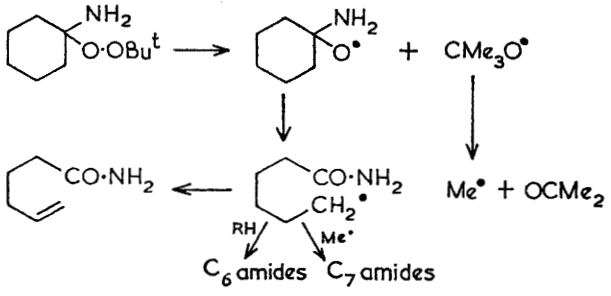
(I)

gave a product which gradually decomposed when fractionated, with loss of t-butyl hydroperoxide; one of the higher-boiling reaction products showed an ion *m/e* 177 ($C_{12}H_{19}N$) in its mass spectrum, probably due to similar loss of t-butylhydroperoxide from the peroxy-imine (II).



(II)

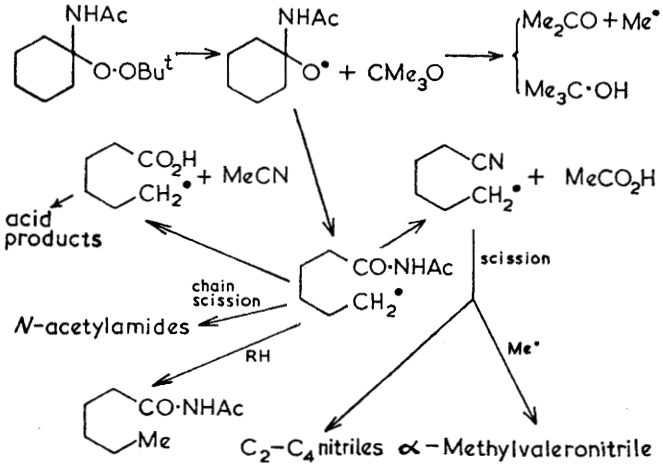
At 160—180° the peroxy-amine (I) decomposed largely to cyclohexanone and t-butyl alcohol, but pyrolysis at 450—550° evidently brought about homolytic fission of the O–O bond with subsequent scission of C–C bonds and methylation by methyl radicals derived from the t-butoxy-radicals, to give C_6 and C_7 saturated amides, a C_6 unsaturated amide, and acetone:



The peroxy-amine (I) lost ammonia and was reconverted into cyclohexanone when heated with sodium methoxide. The peroxy-amine underwent the reactions of a normal amine; thus, reaction with phenyl isocyanate provided a solid phenylurea derivative (III), whilst acetyl chloride, benzoyl chloride, and ethyl chloroformate gave the *N*-acetyl (IV), *N*-benzoyl (V), and carbamate (VI) derivatives respectively; the derivatives from t-butyl hypochlorite (VII) and toluene-*p*-sulphonyl chloride (VIII) failed to crystallize.

R = CO·NHPL (III)
= Ac (IV)
= Bz (V)
= CO·OEt (VI)
= Cl (VII)
= $SO_2 \cdot C_6H_4Me$-*p* (VIII)

Pyrolysis of the *N*-acetyl derivative (IV) at 450°/150 mm. gave rise to a very large number of products including C_2, C_3, and C_4 nitriles (saturated and unsaturated), acetone, t-butyl alcohol acetic acid, cyclohexanone, acetamide, α-methylvaleronitrile, a C_5 branched-chain acid, hexanoic acid, and a mixture of the *N*-acetyl derivatives of butyramide, valeramide, and hexanoamide. The identification of these compounds was based on gas-phase chromatographic separation and spectroscopic examination. The formation of a number of these products can be explained on the basis of initial fission of the t-butoxy-radical (to give acetone, methyl radicals, and t-butyl alcohol) followed by opening of the C_6 ring, rearrangement of the imide to acetic acid and nitrile, and scission of the C_6 chain accompanied by proton transfer and addition of methyl radicals.



[1] Part XII, E. G. E. Hawkins, preceding paper.

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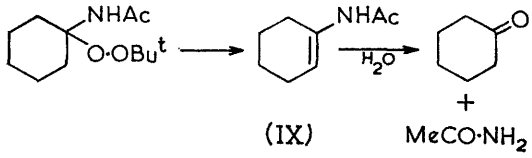
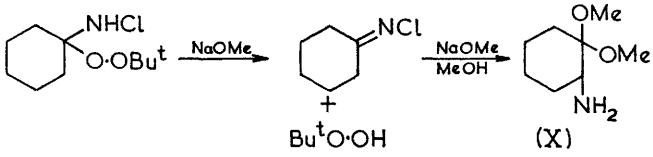
Treatment of the *N*-acetyl derivative (IV) with sodium methoxide produced cyclohexanone, acetamide, ammonia (and presumably t-butyl hydroperoxide as an initial product); when this reaction was carried out at room temperature (very slow) the product contained material thought to be *N*-acetylcyclohex-1-enamine (IX), similar to a product isolated from the direct reaction of (I) with acetyl chloride.



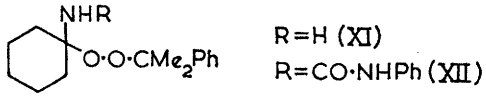
Similar reaction of the *N*-phenylurea (III) with sodium methoxide yielded cyclohexanone, phenylurea, and diphenylurea, whilst the crude *N*-chloro-t-butylperoxycyclohexylamine (VII) yielded 2,2-dimethoxycyclohexylamine (X) *via* *N*-chlorocyclohexylimine by the Neber reaction.[2-4] The compound (X) was also produced by



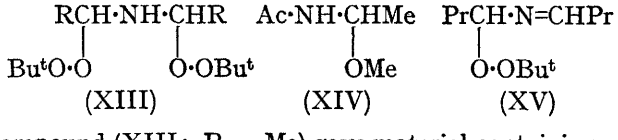
the direct reaction of the chloroimine with sodium methoxide.

The crude *N*-toluenesulphonyl derivative (VIII) with sodium methoxide yielded mainly cyclohexanone and sodium toluene-*p*-sulphonate.

Treatment of cyclohexanone with ammonia and cumyl hydroperoxide gave a crude product which contained the corresponding 1-cumylperoxycyclohexylamine (XI), as shown by the isolation of the phenylurea derivative (XII), and this decomposed on attempted distillation; no attempt was made to purify this amino-peroxide by alternative means.



The reaction of acetaldehyde with ammonia and t-butyl hydroperoxide gave a poor yield of a low-melting solid the elemental analysis, peroxide and amine equivalents, and i.r., n.m.r. and mass spectra, of which were consistent with structure (XIII; R = Me), *i.e.* 1,1′-di-t-butylperoxydiethylamine. With sodium methoxide the



compound (XIII; R = Me) gave material containing *ca.* 60% of a component, separated by gas-phase chromatography, with i.r. and mass spectra consistent with the structure (XIV). Such a product is of interest in that it suggests Kornblum–de la Mare base-catalysed decomposition [5] of one of the secondary–tertiary peroxide systems occurs but in the second simple replacement of t-butylperoxy-group by methoxy-group occurs.

When acetaldehyde was replaced by n-butyraldehyde a mixture of products was obtained which, from analytical and spectroscopic evidence, seemed to consist of the corresponding 1,1′-di-t-butylperoxydibutylamine (XIII; R = Pr) and the peroxy-imine (XV); it is likely that (XIII) is partly converted into (XV) during distillation. Treatment of this product with triethylamine led to the formation of n-butyramide.

No comparable reaction appeared to occur when an acyclic ketone (ethyl methyl ketone or diethyl ketone) was treated with t-butyl hydroperoxide and ammonia; in one experiment unchanged ethyl methylketone was recovered after a 2 month reaction period.

EXPERIMENTAL

Preparation of 1-*t-Butylperoxycyclohexylamine* (I).—Cyclohexanone (70 g.), 70% t-butyl hydroperoxide (100 g.), ammonia (*d* 0·880; 105 c.c.), and ethanol (100 c.c.) were mixed, with cooling, the solution saturated with gaseous ammonia and stored at 0° overnight. The solution was extracted with ether and the ethereal extract was distilled (without a column) to give cyclohexanone, t-butyl hydroperoxide, and a fraction (66·1 g.), b.p. 43—46°/1·0 mm. (peroxide equiv., 187; amine equiv., 225). Refractionation from a Widmer flask gave a fraction of 1-*t-butylperoxycyclohexylamine*, b.p. 36—38°/0·5 mm. (Found: C, 63·8; H, 11·2; N, 6·8; $C_{10}H_{21}NO_2$ requires C, 64·2; H, 11·2; N, 7·5%). With phenyl isocyanate in light petroleum at room temperature it provided a *phenylurea* derivative, m.p. 123—125° (from cold ether) (Found: C, 66·4; H, 8·5; N, 9·35%; peroxide equiv., 302·5. $C_{17}H_{26}N_2O_3$ requires C, 66·6; H, 8·5; N, 9·15%; peroxide equiv., 306). If the peroxy-amine and phenyl isocyanate in light petroleum (b.p. 60—80°) were heated under reflux, mixtures of solid products were isolated which, from mass spectroscopic examination, were shown to contain the phenylurea derivative of cyclohex-1-enylamine [*m/e* 216 ($C_{13}H_{16}N_2O$)] and phenylurea [*m/e* 136 ($C_7H_8N_2O$)].

Reactions of 1-*t-Butylperoxycyclohexylamine.*—(a) *Reaction with sodium methoxide.* The peroxy-amine (5 g.) was added to a solution of sodium (1 g.) in methanol (20 c.c.) and the solution was heated under reflux until no peroxide remained (2 hr.); copious ammonia evolution occurred during the reaction. The solution was diluted with water and extracted with chloroform. Distillation of the extract yielded cyclohexanone (1·1 g.) and a fraction (0·3 g.) containing cyclohex-1-enylcyclohexanone (by i.r. spectroscopy).

(b) *Pyrolysis.* (i) The peroxy-amine (5 g.) was gradually run into a flask heated to 160—180°; it rapidly decomposed and darkened. Distillation gave fractions: (i) (1·6 g.), b.p. 80—120°/760 mm.; (ii) (0·7 g.), b.p. 40—50°/15 mm.; (iii) (0·4 g.), b.p. <220°/15 mm.; and a hard, black residue (0·9 g.). By i.r. spectroscopy, fraction (i) was shown to be

[2] H. E. Baumgarten and F. A. R. Bower, *J. Amer. Chem. Soc.*, 1954, **76**, 4561.
[3] G. H. Alt and W. S. Knowles, *J. Org. Chem.*, 1960, **25**, 2047.
[4] E. Schmitz, *Angew. Chem.*, 1961, **73**, 23.
[5] N. Kornblum and H. E. de la Mare, *J. Amer. Chem. Soc.*, 1951, **73**, 880.

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mainly t-butyl alcohol; fraction (ii) to be mainly cyclohexanone; fractions (iii) contained cyclohexenylcyclohexanone and primary amides.

(ii) The peroxy-amine (10 g.) was slowly dropped into a heated tube, partly packed with glass beads, at 550°/150 mm., during 1 hr. in a slow stream of nitrogen. Distillation of the product gave fractions: (i) (1·4 g.), b.p. 65—72°/760 mm.; (ii) (2·0 g.), b.p. 72—100°/760 mm.; (iii) (1·4 g.), b.p. 120—150°/13 mm.; (iv) (0·3 g.), b.p. 150—230°/13 mm.; and residue (1·0 g.). I.r. spectroscopic examination showed that fraction (i) consisted largely of acetone; fraction (ii) was a mixture of acetone and cyclohexanone; fraction (iii) and fraction (iv) were mainly mixtures of primary amides (with some nitrile and acid), shown by mass spectroscopy to contain unsaturated and saturated C_6 and C_7 amides [*m/e* 113 ($C_6H_{11}NO$), 115 ($C_6H_{13}NO$), and 129 ($C_7H_{15}NO$)] with the C_7 amide probably branched (*e.g.* $C_4H_9CHMe{\cdot}CONH_2$).

(c) *Acetylation.* A solution of the peroxy-amine (38 g.) in ether (120 c.c.) and triethylamine (30 g.) was cooled to −10° and a solution of acetyl chloride (24 g.) in ether (30 c.c.) was gradually added, with the temperature kept at <5°. When the reaction was complete (no further heat produced) the mixture was stirred at room temperature for ½ hr., diluted with water, and extracted with ether. Distillation of the extract gave a fraction (20·0 g.), b.p. 110—115°/0·1 mm., which crystallised on storage. Recrystallised from light petroleum it provided N-*acetyl*-1-*t-butylperoxycyclohexylamine*, m.p. 64—66° (Found: C, 62·8; H, 10·05; N, 6·2%; peroxide equiv., 230·6. $C_{12}H_{23}NO_3$ requires C, 62·9; H, 10·05; N, 6·1%; peroxide equiv., 229).

(d) *Benzoylation.* The peroxy-amine (2 g.) in ether (30 c.c.) and triethylamine (1·5 g.) was treated with benzoyl chloride (1·8 g.) in ether (as above). The ethereal extract was washed with sodium hydrogen carbonate solution, dried, and evaporated. The residue (3·5 g.), recrystallised from light petroleum, gave N-*benzoyl*-1-*t-butylperoxycyclohexylamine*, m.p. 103—105° (Found: C, 70·3; H, 8·7; N, 4·8%; peroxide equiv., 287. $C_{17}H_{25}NO_3$ requires C, 70·1; H, 8·6; N, 4·8%; peroxide equiv., 291).

(e) *Reaction with ethyl chloroformate.* The peroxy-amine (19 g.), in ether (100 c.c.), and triethylamine (15 g.), was stirred at <10° for 2 hr. after addition of ethyl chloroformate (15 g.) in ether; evaporation of the final ethereal extract provided a residue (26 g.) (peroxide equiv., 234·7). Distillation gave *ethyl* 1-*t-butylperoxycyclohexylcarbamate*, b.p. 112—116°/1·0 mm., m.p. 33—34° (from aqueous ethanol) (Found: C, 59·9; H, 9·7; N, 5·35%; peroxide equiv., 252. $C_{13}H_{25}NO_4$ requires C, 60·2; H, 9·65; N, 5·4%; peroxide equiv., 259). The i.r. spectrum had absorption due to =NH, −$NHCO_2R$, and t-butyl; the n.m.r. spectrum provided evidence for −CO_2Et, −OBu^t, and exchangeable proton (N*H*) and *gem*-substituted cyclohexane ring; the mass spectrum showed a weak molecular ion *m/e* 259 ($C_{13}H_{25}NO_4$) and a strong ion *m/e* 170 ($C_9H_{16}NO_2$; loss of t-BuO·O−).

Pyrolysis of this carbamate (10 g.) at 450°/150 mm. during 1 hr. gave, on distillation of the product, acetone, cyclohexanone, a fraction (1·3 g.) shown to contain an unsaturated carbamate (by i.r. spectroscopy), probably ethyl cyclohex-1-enylcarbamate [*m/e* 169 ($C_9H_{15}NO_2$)], and a fraction (1·2 g.) which contained some of this unsaturated carbamate in addition to compounds with primary and secondary amide functions.

(f) *Reaction with t-butyl hypochlorite.* The amino-peroxide (20 g.), in benzene (50 c.c.), was treated with a solution of t-butyl hypochlorite (11 g.), in benzene (20 c.c.), at <5°, the solution being stirred at room temperature for 1 hr. and solvent removed at 20° (initially at 15 mm. then at 0·5 mm.). The residue (22·2 g.), consisting largely of N-*chloro*-1-*t-butylperoxycyclohexylamine* (Found: active oxygen equiv., 111·0. $C_{10}H_{20}ClNO_2$ requires active oxygen equiv., 110·8), was unstable to heat and could not be distilled.

The crude chloroperoxy-amine (11·1 g.) was added to a solution of sodium (3 g.) in methanol (45 c.c.); a moderately vigorous reaction occurred and sodium chloride was precipitated. The solution was heated under reflux for 2 hr. (no active oxygen remained), cooled, water was added and the product was extracted with chloroform. Distillation at 15 mm. gave fractions: (i) (2·6 g.), b.p. 100—110°; (ii) (0·9 g.), b.p. 110—150°; (iii) (0·6 g.), b.p. 150—170°; and residue (0·3 g.). I.r. spectroscopy showed that all three fractions contained the same major component, with ether and amine groups, although fraction (iii) had also compounds with C=N. This major component was separated by gas-phase chromatography and examined by i.r., n.m.r. and mass spectroscopy; the spectra agreed with a structure 2,2-dimethoxycyclohexylamine [*m/e* 159 ($C_8H_{17}NO_2$)], identical with that obtained (70% yield) by treatment of *N*-chlorocyclohexylimine with an excess of warm sodium methoxide. The other components present in fraction (iii) had *m/e* 192 ($C_{12}H_{20}N_2$) and 239 ($C_{14}H_{25}NO_2$).

Treatment of the crude chloroperoxy-amine with a molar amount of sodium methoxide solution at 0° (overnight), followed by extraction with chloroform, gave an extract containing *ca.* 53% of the original active oxygen. Distillation of the extract at 0·1 mm. gave t-butyl hydroperoxide and *N*-chlorocyclohexylimine (identical with authentic material, by i.r. spectroscopy).

(g) *Reaction with toluene*-p-*sulphonyl chloride.* The peroxy-amine (I) (15 g.), dissolved in ether (100 c.c.) and triethylamine (11·5 g.), was treated with a solution of toluene-*p*-sulphonyl chloride (19·5 g.) in ether (50 c.c.); stirring was continued for 1½ hr. The triethylamine hydrochloride was removed by washing the solution with water, and the dried ethereal extract was evaporated at <10° to provide the crude toluene-*p*-sulphonylperoxy-amine.

The crude product (thermally unstable) was gradually added to a solution of sodium (3 g.) in methanol (50 c.c.) at 20—27°; a white solid (10·9), shown to be sodium toluene-*p*-sulphonate, separated. The filtrate was stored at room temperature overnight, and, since it still contained *ca.* 80% of the original active oxygen (probably as free t-butyl hydroperoxide), it was heated under reflux for 5 hr., cooled, and extracted with chloroform. Distillation of the extract at 15 mm. gave fractions: (i) (1·9 g.), b.p. 40—80°; (ii) (0·9 g.), b.p. 80—105°; (iii) (1·7 g.), b.p. 160—210°; and residue (0·5 g.). By i.r. and mass spectroscopy, fraction (i) was shown to be mainly cyclohexanone; fraction (ii) was shown to contain 45% of a mixture of hexanamide and ω-hexenamide, *ca.* 10% of 1,1,2-trimethoxycyclohexane, and many minor constituents; fraction (iii) had *ca.* 40% of *N*-t-butyltoluene-*p*-sulphonamide, *ca.* 10% of 1,1,2-trimethoxycyclohexane, and many unidentified compounds.

A sample of the crude toluene-*p*-sulphonylperoxy-amine (prepared as above) spontaneously decomposed at room temperature and from the decomposition product was isolated toluene-*p*-sulphonamide, m.p. 128—131°, and a distillate containing material thought to have the *N*-toluene-*p*-sulphonylcyclohex-1-enylamine structure (i.r. spectrum).

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Reactions of N-*Acetyl*-1-*t-butylperoxycyclohexylamine*.—(a) *Pyrolysis*. A solution of the peroxide (10 g.) in ethanol (25 c.c.) was dropped into a heated tube at 450°/150 mm., in a slow stream of nitrogen, during 1 hr. At the end of the pyrolysis the cooled tube was washed down with further ethanol. The product and washings were combined and distilled to give fractions: (i) (77·9 g.), b.p. <100°/760 mm.; (ii) (0·4 g.), b.p. <60°/11 mm.; (iii) (1·1 g.), b.p. 120—140°/11 mm., (iv) (1·25 g.), b.p. 140—190°/11 mm.; (v) (0·3 g.), b.p. 190—220°/11 mm.; and residue (0·2 g.). Fraction (i), consisting mainly of ethanol, was analysed by gas-phase chromatography; it contained ethanol (97·2%), acetaldehyde (0·03%), acetone (1·7%), t-butyl alcohol (0·05%), ethyl acetate (0·04%), acetonitrile (0·15%), acrylonitrile (0·07%), methacrylonitrile (0·004%), isobutyl formate (?, 0·02%), methyl isobutyrate (0·01%), propionitrile (0·006%), isobutyronitrile (0·003%), n-butyronitrile (0·003%), and but-3-enonitrile (0·005%). Fraction (ii), similarly analysed, contained ethanol (4·6%), t-butyl alcohol (0·4%), acetic acid (20%), α-methylvaleronitrile (43%), and cyclohexanone (10·5%), as well as unidentified peaks. Fraction (iii) contained ethanol (0·6%), t-butyl alcohol (0·2%), α-methylvaleronitrile and cyclohexanone (together, 8·8%), acetamide (26·5%), a C_5 saturated acid (21%), with α-methyl branching, and unidentified peaks. In these chromatographic analyses several of the major components (acetic acid, cyclohexanone, α-methylvaleronitrile, acetamide, and the C_5 acid) were separated and identified by i.r., n.m.r., and mass spectroscopy. Fraction (iv) had an i.r. spectrum very similar to that of fraction (iii), and fraction (v) had CO_2H, CN, $CO{\cdot}NH_2$, and CONH groups. Examination of the higher-boiling fractions by mass spectroscopy showed the presence of ions *m/e* 43 (Ac), 115 (AcNH·COEt), 143 (AcNH·COBu), 157 (AcNH·COC_5H_{11}), and 171 (AcNH·COC_6H_{13}); hexanoic acid was also isolated by extraction of these fractions with sodium hydroxide.

(b) *With Sodium methoxide*. The peroxide (2·9 g.) was heated under reflux with a solution of sodium (1 g.) in methanol (20 c.c.) for 1 hr.; ammonia was liberated during the reaction. The cooled solution was diluted with water, neutralised with hydrochloric acid, and extracted with chloroform. The chloroform extract, on distillation yielded cyclohexanone (0·4 g.), and the aqueous phase, after evaporation and extraction of the residue with ethanol, gave actamide (0·5 g.).

When the peroxide was treated with sodium methoxide solution at room temperature for 2 months (20% of the peroxide unchanged), ammonia was again produced and sodium acetate gradually precipitated from the solution. Distillation of the chloroform extract of the product gave cyclohexanone and a fraction (25% on peroxide), b.p. 130—155°/15 mm., shown by i.r. spectroscopy to be a mixture of acetamide and a compound previously obtained as a by-product in the preparation of *N*-acetyl-1-t-butylperoxycyclohexylamine. This compound, m.p. 60° (Found: C, 68·7; H, 9·5; N, 10·0. $C_8H_{13}NO$ requires C, 69·05; H, 9·35; N, 10·1%) was probably *N*-acetylcyclohex-1-enylamine; the i.r. spectrum showed it to be a secondary amide and the molecular ion *m/e* 139 and mode of fragmentation supported this structure.

Reaction of Cyclohexanone, Ammonia, and Cumyl Hydroperoxide.—A mixture of cyclohexanone (40 g.), cumyl hydroperoxide (60 g.), ethanol (25 c.c.), and ammonia (*d* 0·880; 25 c.c.) was saturated with gaseous ammonia and stored at 0° overnight. The solution was extracted with ether and solvent was removed from the extract to provide a residue (99·6 g.) (peroxide equiv., 311; amine equiv., 419). An attempt to concentrate the peroxy-amine by distillation at 0·5 mm. led to decomposition, with formation of acetophenone, dimethylphenylmethanol, and cyclohexanone.

Overnight treatment of a portion of the crude product with phenyl isocyanate in light petroleum yielded a sticky, brown solid, which, recrystallised from ether, gave the *phenylurea derivative* of 1-α-*cumylperoxycyclohexylamine*, m.p. 124—125° (Found: C, 71·25; H, 7·65; N, 7·5%; peroxide equiv., 361. $C_{22}H_{28}N_2O_3$ requires C, 71·75; H, 7·6; N, 7·6%; peroxide equiv., 368).

Reaction of Acetaldehyde, Ammonia, and t-Butyl Hydroperoxide.—Acetaldehyde (9 g.) was treated at <−5° with 70% t-butyl hydroperoxide (26·6 g.) and ammonia (*d* 0·880; 20 c.c.) (exothermic), and the solution was stored at 0° overnight after saturation with gaseous ammonia. Extraction with ether, followed by distillation of the extract gave, in addition to unchanged aldehyde and hydroperoxide, a fraction (4·8 g.), b.p. 35—37°/0·5 mm. (peroxide equiv., 126·3; amine equiv., 271·4). Redistillation provided a somewhat purer fraction (2·4 g.), b.p. 67—68°/15 mm. (peroxide equiv., 124·9; amine equiv., 242·2), which solidified on storage at −20°. The solid 1,1′-*di-t-butylperoxydiethylamine* (XIII; R = Me) was filtered off and washed with cold light petroleum; it had m.p. 34—35·5° (Found: C, 57·45; H, 10·8; N, 5·65%; peroxide equiv., 126·2; amine equiv., 254. $C_{12}H_{27}NO_4$ requires C, 57·8; H, 10·85; N, 5·6%; peroxide equiv., 124·5; amine equiv., 249). The i.r. spectrum confirmed the presence of t-butylperoxy and secondary amine groups; the mass spectrum showed only fragment ions *m/e* 90 ($Bu^tO{\cdot}OH$), 86 (C_4H_8NO), 85 (C_4H_7NO), 74 (Bu^tOH) and 70 (C_4H_8N).

Reaction of (XIII; R = Me) *with Sodium Methoxide*.—The peroxy-amine (6·0 g.) was added to a solution of sodium (1 g.) in methanol (30 c.c.); an exothermic reaction occurred and in ¼ hr. no peroxide remained. The cooled solution was diluted with water and extracted with chloroform. Distillation of the extract provided distillate (1·6 g.), b.p. 100—105°/15 mm. and residue (0·2 g.). The distillate was separated by gas-phase chromatography, and apart from small amounts of paraldehyde and acetamide the major component (60%) had i.r. absorption corresponding to secondary amide and ether functions and (in the mass spectrum) a fragment ion *m/e* 102 ($C_4H_8NO_2$) consistent with the structure *N*-(1-methoxyethyl)acetamide (by loss of CH_3).

Reaction of n-Butyraldehyde, Ammonia, and t-Butyl Hydroperoxide.—70% t-Butyl hydroperoxide (53·2 g.) was gradually added, at <0°, to n-butyraldehyde (28 g.), and the mixture was treated with ammonia (*d* 0·880; 40 c.c.), saturated with gaseous ammonia, and stored at 0° overnight. Extraction with ether, followed by distillation of the extract, provided a number of fractions including: (i) (10·2 g.), b.p. 57—57·5°/0·5 mm. (Found: C, 64·65; H, 11·6; N, 5·45%; peroxide equiv., 184; amine equiv., 291), and (ii) (6·8 g.), b.p. 74—76°/0·7 mm. (Found: peroxide equiv., 225; amine equiv., 234). In a similar preparation, starting with n-butyraldehyde (36 g.), a fraction (23·4 g.), b.p. 53·5—56·5°/0·4 mm. (Found: C, 65·45; H, 11·3; N, 6·3%; peroxide equiv., 210·6; amine equiv., 231·8), was obtained, similar to fraction (ii) above. The i.r. spectra of these fractions were somewhat similar, with evidence for C=N,

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$Bu^tO{\cdot}O^-$ and =NH groups, and the n.m.r. spectra indicated the groups Bu^tO, $MeCH_2CH_2$, CHX–N, N=$CHCH_2$ and an exchangeable proton (N*H*). These data suggested that the fractions consisted of mixtures of 1,1′-di-t-butylperoxydibutylamine ($C_{16}H_{35}NO_4$ requires C, 62·9; H, 11·5; N, 4·6%; peroxide equiv., 152·5; amine equiv., 305) and *N*-n-butylidene-1-t-butylperoxybutylamine ($C_{12}H_{25}NO_2$ requires C, 67·0; H, 11·65; N, 6·5%; peroxide and amine equiv., 215).

Fraction (ii) (5 g.) was added to triethylamine (10 g.) and the solution was heated under reflux for 3¼ hr., when no peroxide remained. Distillation at 15 mm. gave, in addition to solvent, fractions: (i) (0·5 g.), b.p. 90—110°; (ii) (1·4 g.), 110—140°; (iii) (1·3 g.), b.p. 140—220°; and residue (0·4 g.). Both fraction (i) and fraction (ii), on trituration with ether, yielded n-butyramide, m.p. and mixed m.p. 112—114°. I.r. spectroscopy showed that these fractions contained t-butyl alcohol in addition to butyramide, and fraction (iii) was a complex mixture, with butyramide, secondary amides, and compounds with the t-butyl group.

Reaction of Ethyl Methyl Ketone, Ammonia, and t-Butyl Hydroperoxide.—A mixture of the ketone (7·2 g.), 70% t-butyl hydroperoxide (13 g.), and ammonia (*d* 0·880; 10 c.c.) was saturated with gaseous ammonia and stored overnight at 0°. Distillation of the ethereal extract at 1·0 mm. gave only t-butyl hydroperoxide, with no higher-boiling fraction. In a similar experiment the reaction mixture was stored at 0°, one portion for 6 days and another for 2 months; work up gave only t-butyl hydroperoxide and ethyl methyl ketone.

Reaction of Diethyl Ketone, Ammonia, and t-Butyl Hydroperoxide.—A mixture of diethyl ketone (17·2 g.), 70% t-butyl hydroperoxide (26·6 g.), and ammonia (*d* 0·880; 20 c.c.), saturated with gaseous ammonia at 0°, was stored at 0° for 4 days. Distillation of the ethereal extract gave t-butyl hydroperoxide and diethyl ketone.

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