

Anal. Calcd. for $C_{12}H_{16}N_4O_7$: C, 44.14; H, 5.13. Found: C, 43.90; H, 4.91.

The picrylsulfonate was obtained from amine and picrylsulfonic acid in isopropyl alcohol. After recrystallization from ethanol containing a little water, the melting point was 194.5–195° (dec.).

Anal. Calcd. for $C_{12}H_{16}N_4O_9S$: C, 36.73; H, 4.11. Found: C, 36.97; H, 4.22.

Cyclobutene from Cyclobutyltrimethylammonium Hydroxide.—Willstätter and von Schmaedel²⁰ prepared cyclobutene from cyclobutyltrimethylammonium hydroxide but did not give experimental details.

To 10 g. (0.1 mole) of cyclobutyltrimethylamine dissolved in 100 ml. of ether was added 16.5 g. (0.11 mole) of methyl iodide. Heat was evolved and the quaternary iodide began to crystallize at once. The mixture was allowed to stand in a refrigerator overnight. The yield of the quaternary iodide was quantitative.

A solution of 25 g. (0.1 mole) of the quaternary salt in 100 ml. of water was shaken with 0.30 mole of freshly prepared silver oxide for two hours. The mixture was filtered and concentrated under reduced pressure. The sirupy quaternary hydroxide was added dropwise to a flask heated to 140° with an oil-bath. The pressure within the flask was maintained at 50 mm. The evolved gases were bubbled through a 1 *N* solution of hydrochloric acid and then condensed in a Dry Ice-cooled trap. The contents of the trap were allowed to evaporate into a gas holder. The yield of cyclobutene calculated from the gas volume was 0.073 mole (73%). The infrared spectrum of the product is shown in Figs. 1 and 2.

The contents of the hydrochloric acid bubbler were made basic and extracted with xylene. The xylene extracts were dried over sodium hydroxide and distilled from sodium. The recovery of cyclobutyltrimethylamine, b. p. 98–102° was 2.8 g. (23%).

Cyclobutene from Cyclobutyltrimethylamine Oxide.—To an ice-cooled stirred mixture of 20 ml. of 35% hydrogen peroxide and 50 ml. of water was added 10 g. (0.1 mole) of cyclobutyltrimethylamine at such a rate as to keep the temperature of the reaction mixture below 10°. The solution was allowed to warm to room temperature and left

overnight. Platinum foil was added to decompose the excess peroxide and the solution was concentrated under reduced pressure.

The sirupy amine oxide was decomposed at 160° as described above for cyclobutyltrimethylammonium hydroxide. The yields of cyclobutene were 50–60%. From 28–32% of cyclobutyltrimethylamine, b. p. 98–102°, was recovered from the hydrochloric acid bubbler. The infrared spectrum of the cyclobutene prepared from the amine oxide pyrolysis is shown in Fig. 1.

Cyclobutyltrimethylamine oxide picrylsulfonate was prepared from the amine oxide and picrylsulfonic acid in isopropyl alcohol; m. p. 168.8–169.5°, after recrystallization from isopropyl alcohol.

Anal. Calcd. for $C_{12}H_{16}O_{10}N_4S$: C, 35.29; H, 3.95. Found: C, 35.24; H, 4.06.

Summary

Cyclobutanone has been prepared in good yield by hydroxylation of methylenecyclobutane with performic acid and cleavage of the resulting glycol with lead tetracetate.

Cyclobutanone has been converted to cyclobutane by the Wolff-Kishner reaction, cyclobutanol by reduction with lithium aluminum hydride, and cyclobutyltrimethylamine by reductive amination with methylamine followed by methylation with formaldehyde and formic acid.

O-Cyclobutyl S-methyl xanthate on pyrolysis gives 1,3-butadiene. Under similar conditions, O-cyclopentyl S-methyl xanthate gives cyclopentene.

Cyclobutene, free of 1,3-butadiene, was prepared by the pyrolysis of cyclobutyltrimethylammonium hydroxide and cyclobutyltrimethylamine oxide.

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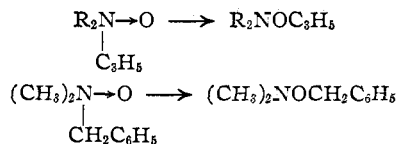
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Thermal Decomposition of Amine Oxides to Olefins and Dialkylhydroxylamines^{1,2}

BY ARTHUR C. COPE, THEODORE T. FOSTER AND PHILIP H. TOWLE

A number of allyldialkylamine oxides and benzyltrimethylamine oxide recently have been shown to rearrange to trialkylhydroxylamine derivatives on heating at temperatures of 80 to 165°, with migration of the allyl and benzyl groups from nitrogen to oxygen.³ In extending this work, it has



been found that N,N-dimethyl-(α -phenylethyl)-amine oxide (I) does not rearrange in this manner

on heating, but undergoes an entirely different type of reaction, forming styrene and N,N-dimethylhydroxylamine. This paper reports an investigation of the thermal decomposition of several amine oxides, homologs of I, which was undertaken to obtain information concerning the scope and nature of the elimination reaction leading to olefins. Mamlock and Wolfenstein⁴ have reported that tri-*n*-propylamine oxide decomposes on heating into propylene and N,N-di-*n*-propylhydroxylamine, but the reaction has received little attention.

N,N-Dimethyl-(α -phenylethyl)-amine oxide (I) was prepared by oxidation of the tertiary amine with 35% aqueous hydrogen peroxide at room temperature, and the excess hydrogen peroxide was decomposed catalytically in the presence of platinum foil. Preparation of the picrate of I from an aliquot of the aqueous solution showed that the

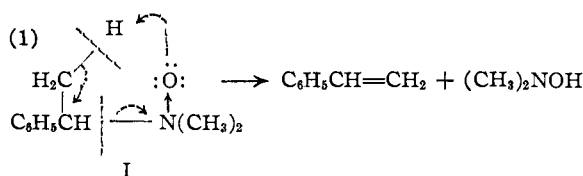
(1) Supported in part by the Office of Naval Research under Contract N5ori-07822, Project Designation NR-055-96.

(2) Presented in part at the St. Louis meeting of the American Chemical Society, Division of Organic Chemistry, September 7, 1948.

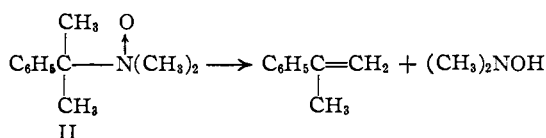
(3) Cope and Towle, *THIS JOURNAL*, **71**, 3423 (1949).

(4) Mamlock and Wolfenstein, *Ber.*, **33**, 159 (1900).

yield of I obtained by oxidation was 98%. After removal of the water from the solution of I by distillation under reduced pressure, the non-volatile amine oxide on heating at 85–115° and 5 mm. pressure was converted into volatile products which collected as a distillate. The distillate was separated by extraction with hydrochloric acid into N,N-dimethylhydroxylamine (isolated in 94% yield as the hydrochloride) and styrene (isolated in 70% yield and characterized as the dibromide). There was no evidence of partial isomerization of I into the rearrangement product, O-(α -phenylethyl)-N,N-dimethylhydroxylamine. This elimination reaction resembles the thermal decomposition of trimethylalkylammonium hydroxides into olefins, trimethylamine and water (Hofmann exhaustive methylation), which proceeds by attack of hydroxyl ion on hydrogens beta to the nitrogen linkage.⁵ The conversion of I to styrene can be formulated in a similar way. The process is represented as intramolecular, but an equivalent intermolecular route is equally in accord with the facts known at present.



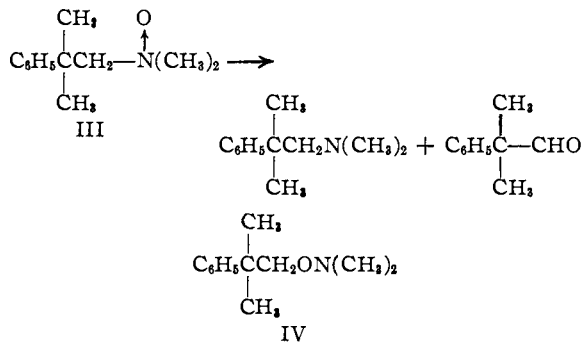
In order to obtain evidence concerning the validity of this interpretation, homologs of I containing no α - and no β -hydrogen atoms were investigated. N,N-Dimethyl-(α,α -dimethylbenzyl)-amine was prepared from benzyl cyanide by methylation, hydrolysis of the α,α -dimethylbenzyl cyanide to α,α -dimethylphenylacetamide, and degradation of the amide to α,α -dimethylbenzylamine by the Hofmann reaction, followed by methylation with formaldehyde and formic acid. Oxidation of the tertiary amine with 35% hydrogen peroxide gave N,N-dimethyl-(α,α -dimethylbenzyl)-amine oxide (II), from which the crystalline picrate was obtained in 96% yield (based on the tertiary amine). II decomposed readily on heating at 75–85° into α -methylstyrene (isolated in 78% yield and characterized as the nitrolpiperidine derivative) and N,N-dimethylhydroxylamine (isolated in 63% yield as the hydrochloride). Occurrence of the elimination with II indicates that α -hydrogen atoms are unnecessary for the reaction. There was no evidence of partial rearrangement of II into O-(α,α -dimethylbenzyl)-N,N-dimethylhydroxylamine.



A related amine with no β -hydrogens, N,N-di-

(5) Hanhart and Ingold, *J. Chem. Soc.*, 997 (1927).

methyl-(β -phenylisobutyl)-amine, was prepared by the Friedel-Crafts alkylation of benzene with β -methylallyldimethylamine.⁶ N,N-Dimethyl-(β -phenylisobutyl)-amine oxide (III) was prepared by oxidation of the tertiary amine with 35% hydrogen peroxide. III was isolated as a crystalline hydrate, and proved to be much more stable than I or II. It did not decompose on heating until a temperature of 148° was reached, at which temperature exothermic decomposition occurred. From the decomposition products were isolated 39% of the original tertiary amine, N,N-dimethyl-(β -phenylisobutyl)-amine, and 7.7% of α,α -dimethylphenylacetaldehyde, identified as the semicarbazone and by oxidation to α,α -dimethylphenylacetic acid. A smaller amount (4.4%) of a weakly basic compound was isolated, which was not obtained completely pure, but from an approximate analysis, solubility characteristics and physical properties was probably the rearrangement product, O-(β -phenylisobutyl)-N,N-dimethylhydroxylamine (IV). The formation of IV by



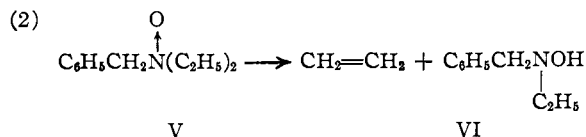
rearrangement could occur in a manner analogous to the rearrangement of benzyldimethylamine oxide,³ even though the α -carbon of the β -phenylisobutyl group is less electron attracting than the α -carbon of a benzyl group, because the elimination reaction is blocked by the absence of β -hydrogens. Decomposition of samples of III at atmospheric pressure produced relatively small amounts of gas, which contained carbon dioxide and oxygen. Other products must have been formed to account for the remainder of III, but they were not isolated. The relative stability of III (compared to I and II) and the fact that III did not decompose to yield an olefin (possible only with rearrangement such as occurs in the dehydration of neopentyl alcohol) furnishes evidence that the elimination proceeds by attack of the amine oxide oxygen on a β -hydrogen atom, as shown in equation (1). A similar decomposition of N-methyl and N-ethyltetrahydroquinoline oxides has been reported by Dodonov⁷ to yield tetrahydroquinoline and formaldehyde and acetaldehyde, respectively.

The behavior of benzyldiethylamine oxide (V) on heating proved to be interesting in that both

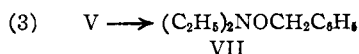
(6) Weston, Ruddy and Suter, *THIS JOURNAL*, **65**, 674 (1943).

(7) Dodonov, *J. Gen. Chem. (U. S. S. R.)*, **14**, 960 (1944); [*C. A.* **39**, 4612 (1945)].

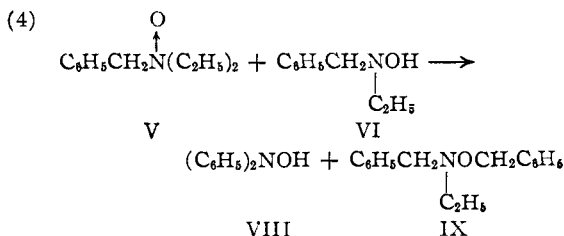
elimination and rearrangement occurred as competitive reactions. Five products were isolated from the decomposition of V. N-Benzyl-N-ethylhydroxylamine (VI), the olefin elimination product, was isolated in 34% yield, and in a separate decomposition at atmospheric pressure the ethylene formed was collected and characterized as ethylene dibromide (14% yield). The rearrange-



ment product, O-benzyl-N,N-diethylhydroxylamine (VII), was isolated in 31% yield (equation 3). Finally, 21% of N,N-diethylhydroxylamine



(VIII) and 16% of O,N-dibenzyl-N-ethylhydroxylamine (IX) were isolated. These products are believed to arise through a bimolecular alkylation reaction (equation 4), in which the amine oxide (V) alkylates the olefin elimination product, N-benzyl-N-ethylhydroxylamine (VI). Alkylation of phenols with replacement of the active hydrogen by a benzyl group has been reported with



benzyltrimethylphenylammonium chloride as the alkylating agent,⁸ and aryl allyl ethers have been prepared with allyldimethylphenylammonium hydroxide as the alkylating agent.⁹ The similarity of the bond between the benzyl group and nitrogen in benzylalkylamine oxides and quaternary ammonium salts and bases containing a benzyl group is apparent, and the ease with which the bond is broken in a nucleophilic displacement reaction presumably accounts for the occurrence of the alkylation reaction (equation 4).

The structures of the products formed by the decomposition and rearrangement of V were determined as follows. N-Benzyl-N-ethylhydroxylamine (VI) was reduced with stannous chloride and hydrochloric acid to benzylethylamine, which was characterized as the hydrochloride and picrate. O-Benzyl-N,N-diethylhydroxylamine (VII) was hydrogenated in the presence of palladium and yielded diethylamine (isolated as the picrate) and benzyl alcohol, which was identified by conversion to benzyl chloride and subsequently to

benzylisothiuronium picrate. O,N-Dibenzyl-N-ethylhydroxylamine (IX) was hydrolyzed in the presence of hydrochloric acid and yielded N-benzyl-N-ethylhydroxylamine (isolated as the picrate) and benzyl chloride, which was converted to benzylisothiuronium picrate. N,N-Diethylhydroxylamine (VIII) was characterized by its physical properties, analysis, analysis of the picrate and conversion to the known hydrochloride and neutral oxalate.

Work is in progress to determine the usefulness of the decomposition of alkyldimethylamine oxides to olefins and dimethylhydroxylamine as a method for the synthesis of olefins compared to the Hofmann exhaustive methylation reaction, and to determine whether the elimination is intramolecular as represented in equation (1), or intermolecular.

Experimental¹⁰

N,N-Dimethyl-(α -phenylethyl)-amine.— α -Phenylethylamine¹¹ was methylated by treatment with formaldehyde and formic acid¹² in 69% yield to N,N-dimethyl-(α -phenylethyl)-amine; b. p. 71° (11 mm.), n_D^{25} 1.5000, d_4^{25} 0.8989; M_D calcd., 48.72; found, 48.83; m. p. of the picrate 140–140.5°.

N,N-Dimethyl-(α -phenylethyl)-amine Oxide (I).—N,N-Dimethyl-(α -phenylethyl)-amine (11.0 g.) was stirred with 18.3 g. (150% excess) of 35% aqueous hydrogen peroxide for eleven hours at room temperature. The excess hydrogen peroxide was decomposed by stirring the mixture with 8 sq. cm. of clean platinum foil until the evolution of oxygen ceased. Most of the water was removed by distillation at 35 mm. pressure and a bath temperature of 45–55°; the distillate and material which condensed in a trap cooled with a mixture of Dry Ice and trichloroethylene in the vacuum line were saved. The residual sirup was diluted with 25 ml. of absolute ethanol, reconcentrated under reduced pressure while nitrogen was admitted through a capillary ebulliator inlet, and the process was repeated twice to remove as much water as possible. The amine oxide remained as a viscous sirup, which from its odor contained a small amount of styrene.

N,N-Dimethyl-(α -phenylethyl)-amine oxide picrate was prepared in 98% yield by treating an aliquot of the aqueous solution of the amine oxide with an equivalent amount of picric acid in aqueous solution, and was recrystallized to constant m. p. from 95% ethanol, m. p. 155.5–156.5°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{18}\text{N}_4\text{O}_8$: C, 48.73; H, 4.60; N, 14.21. Found: C, 48.76; H, 4.77; N, 14.19.

Decomposition of N,N-Dimethyl-(α -phenylethyl)-amine Oxide (I).—A 100-ml. round-bottomed flask fitted with a capillary nitrogen inlet and containing the amine oxide was connected by a large-diameter tube to a condenser set for distillation, which led to two receivers in series cooled in a mixture of Dry Ice and trichloroethylene. The system was evacuated to 5 mm. and the flask was immersed in an oil-bath at 85°. The bath temperature was raised slowly to 115° during thirty-five minutes, at which time almost all of the material had distilled. The bath temperature was raised to 150° to complete the distillation; 0.35 g. of a tarry residue remained. The distillate was combined with the distillate obtained in concentration of the amine oxide solution, pentane was added as a solvent, and the mixture was washed with dilute hydrochloric acid. The acid solu-

(10) Melting points are corrected and boiling points are uncorrected. We are indebted to Mr. S. M. Nagy, Mrs. Louise W. Spencer and Mr. F. A. Bauman for analyses.

(11) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 503.

(12) Clarke, Gillespie and Weisshaus, *THIS JOURNAL*, **55**, 4571 (1933).

(8) Baw, *Quart. J. Ind. Chem. Soc.*, **3**, 101 (1926) [*C. A.*, **20**, 3695 (1926)].

(9) Tarbell and Vaughn, *THIS JOURNAL*, **65**, 231 (1943).

tion was extracted with pentane, and the pentane solutions were washed with water until neutral.

The combined aqueous layers containing hydrochloric acid were concentrated under reduced pressure to a crystalline residue, which was dried by adding absolute alcohol and reconcentrating under reduced pressure, and placed in a vacuum desiccator over phosphorus pentoxide. The yield of *N,N*-dimethylhydroxylamine hydrochloride was 6.73 g. (94%), m. p. 101–104° (sealed capillary). A sample which was recrystallized several times from a mixture of absolute ethanol and ether was obtained as hygroscopic white needles, m. p. 106.5–109° (sealed capillary).¹³

Anal. Calcd. for C_2H_5NOCl : C, 24.62; H, 8.27; N, 14.36; Cl, 36.35. Found: C, 24.96; H, 8.24; N, 14.12; Cl, 35.99.

The pentane solution containing the neutral product was dried over magnesium sulfate and concentrated at atmospheric pressure, after addition of a crystal of picric acid as a polymerization inhibitor. Distillation of the residue yielded 5.34 g. (70%) of styrene; b. p. 82–83° (102 mm.), n_D^{20} 1.5424–1.5428. The styrene was identified by conversion to the dibromide, which after recrystallization from 80% ethanol had m. p. and mixed m. p. with a known sample 72.5–73°.

α,α -Dimethylbenzyl Cyanide.—The general procedure of Haller and Bauer¹⁴ was used, except that both methyl groups were introduced in a single alkylation. Benzyl cyanide (1 mole) in 250 ml. of dry ether was added during thirty minutes to a suspension of 2 moles of freshly prepared sodamide in 1 l. of dry ether, with stirring in a 3-l. three-necked flask equipped with a reflux condenser, dropping funnel and slip-sealed Hershberg stirrer. The mixture was heated under reflux and stirred for one hour, after which 2.2 moles of methyl iodide in 350 ml. of dry ether was added during forty minutes, while the mixture was cooled in an ice-bath. An additional 750 ml. of dry ether was added and the mixture was heated under reflux and stirred for one hour. The mixture was allowed to stand overnight, heated under reflux for one additional hour, and cooled. Ethanol was added to destroy small amounts of sodamide above the surface of the liquid, followed by water to dissolve the precipitated sodium iodide. The product was washed with dilute sodium bisulfite and sodium carbonate solutions and water, dried over sodium sulfate, and distilled through a 20 × 1.6 cm. column packed with glass helices; yield 113.5 g. (78%), b. p. 81–82° (2.2 mm.), n_D^{20} 1.5043–1.5055.

α,α,α -Dimethylphenylacetamide was prepared in 74% yield by warming α,α -dimethylbenzyl cyanide with 85% sulfuric acid for three hours,¹⁴ m. p. 150–153°. A sample recrystallized to constant m. p. from absolute ethanol had m. p. 160–161.5° (ref. 14 reports m. p. 160°).

α,α -Dimethylbenzylamine.—Use of a reported procedure for the Hofmann degradation of α,α,α -dimethylphenylacetamide¹⁵ led to recovery of part of the amide, and the following procedure¹⁶ gave a better yield. A solution of 117 g. of sodium hydroxide in 975 ml. of water was placed in a 2-l. three-necked flask and cooled to 0° in an ice-salt bath. Bromine (46.9 g.) was added in portions with stirring, followed by 79.6 g. of α,α,α -dimethylphenylacetamide (m. p. 157.5–159.5°) in small portions during ten minutes, while the solution was at 0°. The suspension was stirred at 0° for seven hours, packed in ice, and allowed to come to room temperature overnight. The mixture was stirred and warmed on a steam-bath for thirty minutes. The product was extracted with ether, the ether solution was dried over sodium sulfate, and the amine hydrochloride was precipitated by introducing dry hydrogen chloride; yield 79.8 g. (95%), m. p. 240–241° (ref. 15 reports m. p. 240°). The amine was liberated with 6 *N* sodium hydroxide, extracted with ether, dried over sodium sulfate and distilled through a 20 × 1.6 cm. helix-packed column; yield 55 g. (83.5%), b. p. 72–73° (8 mm.); n_D^{20} 1.5175–1.5185.

(13) Hepworth, *J. Chem. Soc.*, **119**, 256 (1921), reports m. p. 102°.

(14) Haller and Bauer, *Ann. chim.*, [9] **9**, 8 (1918).

(15) Baker and Ingold, *J. Chem. Soc.*, 263 (1927).

(16) See "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 280.

***N,N*-Dimethyl-(α,α -dimethylbenzyl)-amine.**—*N,N*-Dimethyl-(α,α -dimethylbenzyl)-amine was prepared from 55 g. of α,α -dimethylbenzylamine, 108 g. of 87% formic acid and 92 ml. of 37% formaldehyde solution by a general procedure previously described.¹² The amine was liberated from its hydrochloride, extracted with ether, and distilled through a 20 × 1.6 cm. helix-packed column; yield 62 g. (94%), b. p. 84–87° (11 mm.), n_D^{20} 1.5071, d_4^{20} 0.9176; *M*_D calcd., 53.35; found, 52.96.

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.94; H, 10.51; N, 8.84.

A picrate prepared from a sample of this amine and an equivalent amount of picric acid in 95% ethanol was recrystallized from a mixture of chloroform and ether, m. p. 210–212° (dec.).¹⁷

Anal. Calcd. for $C_{17}H_{20}N_4O_7$: C, 52.04; H, 5.14; N, 14.28. Found: C, 51.86; H, 5.37; N, 14.36.

***N,N*-Dimethyl-(α,α -dimethylbenzyl)-amine Oxide (II).**—*N,N*-Dimethyl-(α,α -dimethylbenzyl)-amine (20 g.) was oxidized with 35% aqueous hydrogen peroxide (36 g.) during twenty-two hours. After decomposition of the excess hydrogen peroxide in the presence of 8 sq. cm. of platinum foil, an aliquot of the aqueous solution was extracted with ether to remove any remaining amine and treated with an equivalent quantity of picric acid in 95% ethanol. The picrate of II precipitated in 96% yield, m. p. 142–143°. It decomposed partially on attempted recrystallization from absolute ethanol, but was analytically pure as originally precipitated.

Anal. Calcd. for $C_{17}H_{20}N_4O_8$: C, 50.00; H, 4.94; N, 13.72. Found: C, 50.23; H, 5.12; N, 13.53.

N,N-Dimethyl-(α,α -dimethylbenzyl)-amine oxide remained as a viscous sirup after concentration in the manner described for preparation of I. II was decomposed in the same manner as I by heating in a nitrogen atmosphere at 3 mm. pressure and a bath temperature of 75–85° for one and one-half hours. The distillation of the volatile products was completed by raising the temperature to 200° briefly; the residue amounted to 1.2 g. The distillate was separated into a neutral and basic fraction in the manner described for isolating the decomposition products of I. The basic fraction yielded 7.5 g. (63%) of *N,N*-dimethylhydroxylamine hydrochloride. Fractionation of the dried pentane extracts yielded 11.3 g. (78%) of α -methylstyrene, b. p. 59–60° (15 mm.). A sample of the α -methylstyrene was characterized by treatment with isomyl nitrite and hydrochloric acid, which yielded the nitrosochloride, which in turn was treated with an excess of piperidine in benzene. The nitropiperidine derivative of α -methylstyrene so obtained was recrystallized from hexane; m. p. and mixed m. p. with a known sample¹⁸ 121–122°.

β -Methylallyldimethylamine and *N,N*-Dimethyl-(β -phenylisobutyl)-amine.— β -Methylallyl chloride (1 mole) was added dropwise with stirring to 4 moles of 25% aqueous dimethylamine solution during two and seven-tenths hours. The temperature of the reaction mixture rose from 24 to 39° from the heat of reaction. The mixture was stirred for two hours, allowed to stand overnight, and made strongly alkaline with 6 *N* sodium hydroxide. The amine was extracted with ether, the ether solution was dried over sodium sulfate, and distilled through a 20 × 1.6 cm. helix-packed column. The yield of β -methylallyldimethylamine⁹ was 81 g. (82%), b. p. 82–83.5°, n_D^{20} 1.4055. Reaction of 49.5 g. of β -methylallyldimethylamine with benzene in the presence of anhydrous aluminum chloride yielded 60.7 g. (69%) of *N,N*-dimethyl-(β -phenylisobutyl)-amine⁹; b. p. 89–90° (9 mm.), n_D^{20} 1.4973–1.4983. A picrate prepared from this amine in 95% ethanol and recrystallized from absolute ethanol had m. p. 176–178.5°.

Anal. Calcd. for $C_{15}H_{22}N_2O_7$: C, 53.20; H, 5.46; N, 13.79. Found: C, 53.31; H, 5.49; N, 13.59.

(17) Dunn and Stevens, [*J. Chem. Soc.*, 281 (1934)], report m. p. 205°.

(18) Perrot, *Compt. rend.*, **203**, 331 (1936), reports m. p. 122°.

N,N-Dimethyl-(β -phenylisobutyl)-amine Oxide (III).—N,N-Dimethyl-(β -phenylisobutyl)-amine (25 g.) was stirred with 33.5 g. of 35% aqueous hydrogen peroxide at room temperature until a clear solution was obtained (forty-eight hours). The excess hydrogen peroxide was destroyed by periodic addition of single drops of Catalase Sarett¹⁹ until no more oxygen was evolved. The aqueous solution was extracted with ether to remove any unreacted amine and concentrated at 25 mm. pressure and a bath temperature of 45–55°. A portion of the white, crystalline solid residue was recrystallized from a mixture of absolute ethanol and ether with considerable loss. Analysis indicated that the solid so obtained was N,N-dimethyl-(β -phenylisobutyl)-amine oxide monohydrate.

Anal. Calcd. for $C_{12}H_{19}NO \cdot H_2O$: C, 68.21; H, 10.02; N, 6.63. Found: C, 67.95; H, 9.68; N, 6.49.

Equivalent quantities of III in water and picric acid in 95% ethanol yielded 98% of the picrate of III, m. p. after recrystallization from absolute ethanol as fine yellow needles 171–172° (dec.).

Anal. Calcd. for $C_{13}H_{22}N_4O_3$: C, 51.18; H, 5.25; N, 13.27. Found: C, 51.01; H, 5.32; N, 13.38.

III prepared from 25 g. of N,N-dimethyl-(β -phenylisobutyl)-amine was decomposed in the apparatus described for decomposition of I, except that a trap cooled with liquid nitrogen was placed between the second receiver and the vacuum pump. The flask containing the amine oxide was immersed in an oil-bath at 95° and then evacuated. The bath was heated slowly to 148° during thirty minutes, at which time decomposition of the amine oxide began and the pressure rose to 30 mm. The heating bath was removed rapidly and replaced after five minutes, when the vigorous decomposition had subsided and the pressure in the system had again fallen to 3 mm. (In other experiments the sudden decomposition blew the wide-bore tube connecting the flask and condenser out of the flask, and it presumably would be safer to conduct the decomposition in an inert, high-boiling solvent to dissipate the heat of reaction.) The oil-bath was heated to 220° during two hours; the residue amounted to 1.6 g. The trap cooled with liquid nitrogen contained only a few drops of condensate, from which no dimethylamine picrate could be isolated.

The distillate was separated into neutral and basic fractions as described under decomposition of I. The residue obtained on concentration of the hydrochloric acid solution was made strongly basic with 6 N sodium hydroxide and extracted with ether. The ether extracts were dried over sodium sulfate and distilled through a 20 \times 1.0 cm. helix-packed column. N,N-Dimethyl-(β -phenylisobutyl)-amine was recovered in a yield of 9.7 g. (39%), b. p. 91–94° (12.5 mm.), and identified by the m. p. of its picrate and mixed m. p. with a known sample, which was not depressed.

The residues from distillation of the recovered amine and from the neutral fraction described below appeared to be identical from preliminary distillations, and were combined and refractionated through a 30 \times 0.8 cm. semimicro column.²⁰ In this way 1.19 g. of a compound was obtained; b. p. 111–115.5° (0.85 mm.), n_D^{25} 1.5322–1.5332. The compound was weakly basic and formed salts with picric acid and picrylsulfonic acid which crystallized poorly and could not be purified. Analytical results were in poor agreement with the formula for O-(β -phenylisobutyl)-N,N-dimethylhydroxylamine (IV), indicating the presence of an impurity if that structure is correct.

Anal. Calcd. for $C_{12}H_{19}NO$: C, 74.56; H, 9.91; N, 7.25. Found: C, 74.69; H, 8.66; N, 7.57.

The pentane solution of the neutral product was dried over magnesium sulfate, concentrated, and distilled through a 20 \times 1.0 cm. helix-packed column. α,α -Dimethylphenylacetaldehyde²¹ was obtained in a yield of 1.6 g. (7.7%); b. p. 98.5° (17 mm.), 217–218° (Siwolo-

boff); n_D^{25} 1.5101, d_4^{25} 0.9854; M_D calcd., 44.80; found, 44.99.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.74; H, 8.11.

The semicarbazone prepared from the aldehyde had m. p. 169–173°, and a sample of the aldehyde which was oxidized with silver oxide yielded α,α -dimethylphenylacetic acid,²² m. p. 76.5–78°. Mixed m. p. of the acid with an authentic sample, m. p. 77.5–78.5°, obtained by the alkaline hydrolysis of α,α,α -dimethylphenylacetamide, was not depressed.

Small samples of N,N-dimethyl-(β -phenylisobutyl)-amine oxide hydrate were decomposed by heating at atmospheric pressure and the relatively small amount of gas which was evolved was collected. It proved to contain carbon dioxide and oxygen, and not to contain dimethylamine (picric acid did not precipitate a picrate).

Benzyl-diethylamine Oxide (V).—Benzyl-diethylamine (50 g.) was stirred with 75 g. of 35% aqueous hydrogen peroxide for seventeen hours, until a homogeneous solution was obtained. Excess hydrogen peroxide was decomposed by stirring the solution with platinum foil. Benzyl-diethylamine oxide picrate, prepared in 95% yield from an aliquot of a similar preparation and picric acid in 95% ethanol and recrystallized from the same solvent, had m. p. 124.5–125°.

Anal. Calcd. for $C_{17}H_{20}N_4O_3$: C, 50.00; H, 4.94; N, 13.72. Found: C, 49.71; H, 5.07; N, 13.70.

The residual sirup of benzyl-diethylamine oxide obtained on concentration was dried and decomposed by heating at 1 mm. in an oil-bath heated from 100 to 180° during one and one-half hours, in the manner described for decomposition of I. In a few cases the amine oxide crystallized before decomposition started. In such cases the flask containing the solid was heated momentarily with a free flame near the edge of the solid until decomposition started, as indicated by a pressure increase from 1 to 30 mm., to prevent a sudden decomposition. The temperature of the oil-bath was raised to 200° briefly; a residue of 1.5 g. remained. The distillate was combined with the material which was distilled during concentration of the amine oxide solution, and pentane was added. The dilute hydrochloric acid extract of the mixture was concentrated, made alkaline with 6 N sodium hydroxide, and extracted with ether, which was dried over sodium sulfate and distilled through a 20 \times 1.0 cm. helix-packed column. The distillation yielded 2.7 g. (21%) of N,N-diethylhydroxylamine (VIII), 9.6 g. (19%) of O-benzyl-N,N-diethylhydroxylamine (VII) and 14.5 g. (34%) of N-benzyl-N-ethylhydroxylamine (VI).

The N,N-diethylhydroxylamine²³ had b. p. 48° (15 mm.), n_D^{25} 1.4173, d_4^{25} 0.8612; M_D calcd., 25.78; found, 26.04.

N,N-Diethylhydroxylamine picrate was prepared in 95% yield in 95% ethanol and recrystallized from benzene, m. p. 95–98°.

Anal. Calcd. for $C_{10}H_{14}N_4O_3$: C, 37.74; H, 4.43; N, 17.61. Found: C, 37.90; H, 4.76; N, 17.53.

N,N-Diethylhydroxylamine hydrochloride proved to be very hygroscopic and was not recrystallized satisfactorily. A sample prepared from VIII in ether and dry hydrogen chloride had m. p. 65–69.5° (sealed capillary).²⁴ The neutral oxalate had m. p. 137–140° after recrystallization from absolute ethanol.²⁵

O-Benzyl-N,N-diethylhydroxylamine (VII) had b. p.

(22) Tiffeneau and Dorlencourt [*Compt. rend.*, **143**, 1244 (1909)], report m. p. 78°; Bistrzycki and Mauron [*Ber.*, **40**, 4371 (1907)], report m. p. 80–81°.

(23) (a) Lachman [*Ber.*, **33**, 1027 (1900)] reports b. p. 47–49° (15 mm.); (b) Bewad [*J. prakt. Chem.*, [2] **63**, 100 (1901)] reports d_4^{20} 0.8670.

(24) Wieland [*Ber.*, **36**, 2317 (1903)] reports m. p. 63°; ref. 13 reports m. p. 63–64°, and ref. 23b reports m. p. 72–73°.

(25) Dunstan and Goulding [*J. Chem. Soc.*, **75**, 800 (1899)] report m. p. 136–137°; Wieland (ref. 24) reports m. p. 138°; ref. 13 reports m. p. 137–138°, and ref. 23b reports m. p. 134–138°.

(19) Vita-Zyme Laboratories, Chicago, Ill.

(20) Gould, Holzman and Niemann, *Anal. Chem.*, **20**, 361 (1948).

(21) Tiffeneau and Orekhoff, *Bull. soc. chim.*, **29**, 809 (1921), report b. p. 215–218°; m. p. of the semicarbazone 176–177°.

70–71° (2.1 mm.), n_D^{25} 1.4891, d_4^{25} 0.9336; M_D calcd. 54.62; found, 55.43.

Anal. Calcd. for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.69; H, 9.64; N, 7.87.

O-Benzyl-N,N-diethylhydroxylamine picrate was prepared in 94% yield in 95% ethanol and had m. p. 115–116° after recrystallization from absolute ethanol.

Anal. Calcd. for $C_{17}H_{20}N_4O_8$: C, 50.00; H, 4.94; N, 13.72. Found: C, 50.06; H, 5.02; N, 13.66.

O-Benzyl-N,N-diethylhydroxylamine hydrochloride was prepared from VII and concentrated hydrochloric acid and recrystallized from a mixture of absolute ethanol and ether: m. p. 107–108°.

Anal. Calcd. for $C_{11}H_{18}NOCl$: C, 61.24; H, 8.41; N, 6.49; Cl, 16.44. Found: C, 61.55; H, 8.59; N, 6.41; Cl, 16.13.

N-Benzyl-N-ethylhydroxylamine (VI) had b. p. 88° (1.1 mm.); n_D^{25} 1.5232, d_4^{25} 1.0097; M_D calcd., 45.27; found, 45.76.

Anal. Calcd. for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.27. Found: C, 71.74; H, 8.94; N, 9.27.

N-Benzyl-N-ethylhydroxylamine picrate was prepared in 95% ethanol and recrystallized from aqueous ethanol, from which it separated as a monohydrate which was dried for five minutes at 35 mm. and room temperature for analysis, m. p. 79–81°.

Anal. Calcd. for $C_{15}H_{16}N_4O_8 \cdot H_2O$: C, 45.23; H, 4.55; N, 14.07; H_2O , 4.52. Found: C, 44.94; H, 4.74; N, 14.09; H_2O (by loss in weight at 55° and 35 mm.), 4.4.

The pentane solution containing weakly basic decomposition products was dried over magnesium sulfate and concentrated. The residue was fractionated through a 20 × 1.0 cm. helix-packed column and yielded an additional 6.0 g. (12%) of O-benzyl-N,N-diethylhydroxylamine (VII); b. p. 66° (1.4 mm.), n_D^{25} 1.4868–1.4872, making the total yield 31%. O,N-Dibenzyl-N-ethylhydroxylamine (IX) was separated as a higher boiling fraction; yield 5.3 g. (16%), b. p. 148° (4 mm.), n_D^{25} 1.5383, d_4^{25} 1.0105; M_D calcd., 74.00; found, 74.64.

Anal. Calcd. for $C_{18}H_{19}NO$: C, 79.63; H, 7.94; N, 5.81. Found: C, 79.78; H, 8.12; N, 5.74.

The picrate of O,N-dibenzyl-N-ethylhydroxylamine was prepared in 95% ethanol and recrystallized from absolute ethanol, m. p. 108.5–109.5°.

Anal. Calcd. for $C_{22}H_{22}N_4O_8$: C, 56.17; H, 4.72; N, 11.91. Found: C, 56.16; H, 4.83; N, 12.01.

A sample of benzyldiethylamine oxide, prepared from 20 g. of benzyldiethylamine and hydrogen peroxide, was decomposed by heating at atmospheric pressure in an oil-bath at 110–180° during one and eight-tenths hours. The ethylene which was formed was collected over sodium chloride solution in a gas buret, and amounted to 1.5 l. The ethylene was bubbled through bromine water and converted to ethylene dibromide, which was washed with water, dried over calcium chloride and distilled; yield 3.26 g. (14%), b. p. 128–130°.

Structure Proof of Compounds Formed by Decomposition of Benzyldiethylamine Oxide. (a) N-Benzyl-N-ethylhydroxylamine (VI).—A solution of 1.19 g. of VI in 10 ml. of 3 *N* hydrochloric acid was treated with 1.77 g. of stannous chloride dihydrate in 5 ml. of concentrated hydrochloric acid. The mixture was warmed on a steam-bath for six hours, diluted with water, and saturated with hydrogen sulfide. The precipitated tin sulfides were separated by filtration, and the filtrate and washings were concentrated under reduced pressure to yield 1.37 g. (102%) of benzyldiethylamine hydrochloride, m. p. 183–184°. Recrystallization from a mixture of absolute ethanol and ether gave white plates of the hydrochloride, m. p. and mixed m. p. with a known sample²⁶ 184–185°. A portion of the benzyldiethylamine hydrochloride was converted into the picrate, which after crystallization from aqueous ethanol

had m. p. and mixed m. p. with a known sample²⁷ 122–123°.

(b) O-Benzyl-N,N-diethylhydroxylamine (VII).—A solution of 0.311 g. of VII in 10 ml. of absolute ethanol was hydrogenated in the presence of 0.3 g. of 10% palladium-on-Norite catalyst for thirty hours, in which time 1.45 molar equivalents of hydrogen was absorbed. The catalyst was separated by filtration, washed with ethanol and the filtrate and washings were distilled at atmospheric pressure until only a small residue remained. Addition of a solution of 0.40 g. of picric acid in 5 ml. of ethanol to the distillate precipitated diethylamine picrate as an oil which was crystallized from benzene. The yield of diethylamine picrate, m. p. 71–73°, was 0.412 g. (79%). A sample which was recrystallized from benzene had m. p. 73.5–74.5° and a mixed m. p. with a known sample was not depressed.

The residue remaining after distillation of the ethanol and diethylamine was warmed on a steam-bath for five minutes with 1 ml. of concentrated hydrochloric acid. The oil which separated was extracted with ether, dried over sodium sulfate and concentrated. Thiourea (0.13 g.) was added to a solution of the residue in 2 ml. of ethanol, and the mixture was warmed on a steam-bath for two minutes. Picric acid (0.4 g.) was added, and the mixture was cooled and diluted with water. Benzyliothiuronium picrate separated in a yield of 0.148 g. (22%), m. p. after recrystallization from aqueous ethanol 187–188.5°, which was not depressed on mixture with a known sample. The low yield of this derivative and the high hydrogen uptake in the catalytic reduction are presumed to be due to partial hydrolysis of the initially formed benzyl alcohol to toluene.

(c) O,N-Dibenzyl-N-ethylhydroxylamine (IX).—IX (0.13 g.) was heated under reflux with 25 ml. of 6 *N* hydrochloric acid for one and eight-tenths hours. The aqueous acid was distilled under reduced pressure, and the oily residue was treated with 0.13 g. of picric acid in 5 ml. of ethanol. After dilution with water to the point of turbidity, the picrate of O,N-dibenzyl-N-ethylhydroxylamine separated. Further dilution of the filtrate precipitated 0.062 g. (20%) of a second picrate, which after recrystallization melted at 76.5–79° and was identified as N-benzyl-N-ethylhydroxylamine picrate monohydrate by mixed m. p. with a known sample, which showed no depression.

In another similar hydrolysis of 0.38 g. of IX, the distillate of aqueous hydrochloric acid was extracted with ether. The extract was dried over sodium sulfate, concentrated, and the residue was warmed on a steam-bath with concentrated hydrochloric acid in the manner described under (b) above. Subsequent treatment with thiourea followed by picric acid as described in (b) yielded 0.10 g. (25%) of benzyliothiuronium picrate, m. p. 186.5–187.5°, which was not depressed by an authentic sample.

Summary

N,N-Dimethyl-(α -phenylethyl)-amine oxide (I) and N,N-dimethyl-(α,α -dimethylbenzyl)-amine oxide (II) undergo an elimination reaction rather than rearrangement on heating at 75–115°, forming N,N-dimethylhydroxylamine in both cases and styrene and α -methylstyrene, respectively. N,N-Dimethyl-(β -phenylisobutyl)-amine oxide (III) does not form an olefin on heating, indicating that the elimination reaction probably proceeds in a manner similar to the Hofmann reaction by attack of the amine oxide oxygen on β -hydrogen atoms (equation 1). Benzyldiethylamine oxide (V) rearranges in part on heating into O-benzyl-N,N-diethylhydroxylamine (VII), and also forms products of the elimination reaction, ethylene and N-benzyl-N-ethylhydroxylamine (VI). Additional products which are formed in this case

(26) Hoover and Hass [*J. Org. Chem.*, **12**, 508 (1947)] report m. p. 184°.

(27) Graymore *J. Chem. Soc.*, 41 (1941), reports m. p. 122–123°.