mosphere at 0.85–0.2 mm. To the distillate was added 40 ml. of ether and the resulting mixture was washed with 10% hydrochloric acid solution, sodium bicarbonate solution and water. The ether solution was dried over magnesium sulfate and distilled through a semimicro column, yielding 0.83 g. (72%) of a mixture of 1- and 3-phenylcyclohexene, b.p. 78° (2.8 mm.), $n^{25}\text{D}$ 1.5432–1.5472, λ 247 mμ, ϵ 738 (95% ethanol). Calculations based on the ultraviolet spectra indicated that the mixture contained 98% of 3-phenylcyclohexene.

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

Amine Oxides. II. Conversion to N,N-Dialkylhydroxylamines[1]

BY ARTHUR C. COPE AND HIOK-HUANG LEE

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Oxidation with peracetic acid has been shown to provide a convenient method for converting relatively unreactive tertiary amines to the amine oxides. The progress of the reaction can be followed by titration to determine loss of active oxygen from the peracetic acid. A series of seven N,N-dialkylhydroxylamines has been prepared in yields of 42–84% by pyrolysis of symmetrical tertiary amine oxides.

The thermal decomposition of N,N-dimethylalkylamine oxides is known to proceed with elimination of a β-hydrogen atom and the amine oxide group, forming an olefin and N,N-dimethylhydroxylamine.[2] In the first reported example of this type of reaction, Mamlock and Wolffenstein[3] described the decomposition of tri-*n*-propylamine oxide on heating, forming propylene and N,N-di-*n*-propylhydroxylamine. This paper reports the preparation and thermal decomposition of a number of *sym*-trialkylamine oxides, forming terminal olefins and N,N-dialkylhydroxylamines.[4]

The low-molecular weight triethylamine and tri-*n*-propylamine were readily converted to the corresponding amine oxides by treatment with 30% aqueous hydrogen peroxide. Completion of the oxidation was indicated by a negative phenolphthalein test for the amines.[2] However, oxidation of the higher homologs tri-*n*-butyl-, tri-*n*-amyl-, tri-isoamyl-, tri-*n*-hexyl- and tri-*n*-heptyl-amine by hydrogen peroxide was found to proceed slowly. Moreover, these amines failed to give a satisfactory color test with phenolphthalein or other common indicators, so that completion of the oxidation could not be determined by spot tests. It has been found possible to oxidize these less reactive tertiary amines conveniently with peracetic acid, and to follow the progress of the oxidations by iodometric titration.[5]

It has been shown previously that aliphatic amine oxides do not oxidize acidified potassium iodide to iodine.[6] It was therefore possible to oxidize tertiary amines with an excess of peracetic acid containing a known amount of active oxygen, and ascertain when the reactions were complete by removing aliquots periodically, adding potassium iodide, and titrating the liberated iodine with standard sodium thiosulfate solution. Five of the amine oxides listed in Table I were prepared by this method, which is recommended in general for the oxidation of relatively unreactive tertiary amines. The hygroscopic amine oxides were not isolated as such, but converted directly to the crystalline picrates.

The usefulness of peracetic acid as an oxidizing agent for high-molecular weight amines is illustrated by the fact that with this reagent tri-*n*-butylamine was essentially completely oxidized in four hours, while oxidation of the same amine with hydrogen peroxide required approximately seventy-two hours. The same yield of the amine oxide picrate was obtained whether or not the calculated amount of sodium acetate was added to neutralize the sulfuric acid present in commercial peracetic acid.

The results of thermal decomposition of the trialkylamine oxides are listed in Table II. The decompositions occurred at 100–150° under reduced pressure, and the N,N-dialkylhydroxylamines and olefins which formed distilled until no more of the relatively non-volatile amine oxides remained. In four cases the 1-alkenes that were formed were isolated and identified by their physical properties, including infrared spectra.

The ease of preparation of the amine oxides and of their thermal decomposition recommend this sequence as a synthetic method for *sym*-N,N-dialkylhydroxylamines. However, unsymmetrical tertiary amine oxides form mixtures of products upon thermal decomposition, since the elimination can involve the β-hydrogen atoms of any alkyl groups that are present.[7] The method of Rogers,[4] employing the thermal decomposition of N-oxides of β-dialkylaminopropionic esters and related compounds, accordingly, appears to be the method of choice for the preparation of unsymmetrical N,N-dialkylhydroxylamines.

Experimental[8]

Trialkylamine Oxides.—Triethylamine, tri-*n*-propylamine and tri-*n*-butylamine were oxidized with 30% aqueous hydrogen peroxide and the excess hydrogen peroxide was decomposed by adding platinum black by essentially the procedure described for preparing N,N-dimethylcyclooöctyl-

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[1] Sponsored by the Office of Ordnance Research, U. S. Army, under Contract No. DA-19-020-ORD-3226, Project TB2-0001 (1112).

[2] A. C. Cope, T. T. Foster and P. H. Towle, THIS JOURNAL, **71**, 3929 (1949).

[3] L. Mamlock and R. Wolffenstein, *Ber.*, **33**, 159 (1900).

[4] M. A. T. Rogers, *J. Chem. Soc.*, 769 (1955), reported a similar investigation shortly after this work was completed.

[5] D. Swern in "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 392.

[6] M. Polonovski and M. Polonovski, *Bull. soc. chim. France*, [4] **39**, 1147 (1926).

[7] A. C. Cope, N. A. Le Bel, H. H. Lee and W. R. Moore, to be published.

[8] Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

TABLE I

TRIALKYLAMINE OXIDES, $R_3N^+{-}O^-$

		Picrate								
					Carbon, %		Hydrogen, %		Nitrogen, %	
R	Oxidant	Yield, %	M.p., °C.	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
C_2H_5	H_2O_2	77	165[a]							
n-C_3H_7	H_2O_2	93	128–129[a]							
n-C_4H_9	H_2O_2	98	110.5–111[b]	$C_{18}H_{30}N_4O_8$	50.22	50.06	7.03	7.02	13.02	13.13
	CH_3CO_3H	95								
n-C_5H_{11}	CH_3CO_3H	99	61.6–63[b]	$C_{21}H_{36}N_4O_8$	53.37	53.57	7.68	7.84	11.86	11.67
i-C_5H_{11}	CH_3CO_3H	93	99–100[b]	$C_{21}H_{36}N_4O_8$	53.37	53.62	7.68	7.87	11.86	11.81
n-C_6H_{13}	CH_3CO_3H	84	51–52[c]	$C_{24}H_{42}N_4O_8$	56.01	56.18	8.23	8.41	10.89	10.62
n-C_7H_{15}	CH_3CO_3H	84	48.2–48.8[b]	$C_{27}H_{48}N_4O_8$	58.12	57.87	8.69	8.53	10.09	9.99

[a] W. R. Dunstan and E. Goulding, *J. Chem. Soc.*, **75**, 1007 (1899), report m.p. 164° for triethylamine oxide picrate and m.p. 129° for tri-*n*-propylamine oxide picrate. [b] Recrystallized from aqueous ethanol. [c] Recrystallized from chloroform–cyclohexane.

TABLE II

THERMAL DECOMPOSITION OF TRIALKYLAMINE OXIDES, $R_3N^+{-}O^-$

		Dialkylhydroxylamines, R_2NOH		
R	1-Alkene Yield, %	Yield, %	M.p., °C.	M.p. of acid oxalate salt, °C.
C_2H_5		69	57 (25 mm.)[a,b]	
n-C_3H_7		84	27–28[c]	139–140[c]
			85–86 (40 mm.)[a]	
n-C_4H_9		79	52–53[d]	144–145[d]
n-C_5H_{11}	65	75	57–58[e,f]	134–134.8[j]
i-C_5H_{11}	53	42	34–35[e,g]	168–170[k]
n-C_6H_{13}	64	70	69–70[e,h]	134.5–135.5[l]
n-C_7H_{15}	76	71	72.8–73.8[i]	137[i]

[a] Boiling point, °C. [b] n^{25}D 1.4173, m.p. of picrate 95–98°; the same values are reported in ref. 2. [c] I. Bewad, *J. prakt. Chem.*, [2] **63**, 94 (1901), reports m.p. 28.5–29.5°. W. R. Dunstan and E. Goulding, *J. Chem. Soc.*, **75**, 792 (1899), report m.p. of acid oxalate 139°. [d] V. H. Dermer and O. C. Dermer, THIS JOURNAL, **64**, 3057 (1942), reported m.p. 52.5–53°, m.p. of acid oxalate 144–144.5°. [e] Recrystallized from aqueous ethanol and sublimed. [f] *Anal.* Calcd. for $C_{10}H_{23}NO$: C, 69.31; H, 13.38; N, 8.08. Found: C, 69.54; H, 13.12; N, 7.95. [g] *Anal.* Calcd. for $C_{10}H_{23}NO$: C, 69.31; H, 13.38; N, 8.08. Found: C, 69.44; H, 13.05; N, 8.07. [h] *Anal.* Calcd. for $C_{12}H_{27}NO$: C, 71.58; H, 13.52; N, 6.96. Found: C, 71.53; H, 13.59; N, 7.06. [i] G. Vavon and Krajcinovic, *Bull. soc. chim. France*, [4] **43**, 231 (1928), report m.p. 74°, m.p. of acid oxalate 137°. [j] Crystallized by dissolving in absolute ethanol and precipitating with ether. *Anal.* Calcd. for $C_{12}H_{25}NO_5$: C, 54.73; H, 9.57; N, 5.32. Found: C, 54.68; H, 9.44; N, 5.27. [k] G. Vavon and Krajcinovic, *Bull. soc. chim. France*, [4] **43**, 231 (1928), report m.p. 167–168° for the neutral oxalate. [l] Recrystallized from ethanol. *Anal.* Calcd. for $C_{14}H_{29}NO_5$: C, 57.71; H, 10.03; N, 4.81. Found: C, 57.49; H, 10.22; N, 4.78.

amine oxide.[9] Completion of the oxidations was indicated by negative spot tests for the amines with phenolphthalein, and completion of the decomposition of hydrogen peroxide by negative tests with lead sulfide paper.[2] The procedures used for the oxidations with peracetic acid are illustrated by the following preparation of tri-*n*-amylamine oxide picrate. A 10-ml. volumetric flask containing 1.475 g. (0.0065 mole) of tri-*n*-amylamine was cooled in an ice–salt-bath and 3 ml. of commercial 40% peracetic acid[10] containing 0.008 mole of active oxygen per milliliter[11] was added dropwise from a pipet. The mixture was shaken thoroughly, allowed to remain in the ice–salt mixture for 0.5 hr., and then at room temperature for 4 hr. The solution was diluted to volume with glacial acetic acid, and a 1-ml. aliquot was cooled and treated with a freshly prepared solution of 4 g. of potassium iodide in 10 ml. of water. A dark brown viscous oil separated and was dissolved by adding 5–10 ml. of carbon tetrachloride. The mixture was stirred with a magnetic stirrer and titrated with 0.1 *N* sodium thiosulfate solution until both the aqueous and carbon tetrachloride layers became colorless. After a small blank correction for the slight decomposition of the standard peracetic acid, under the conditions (time and temperature) of the oxidation, determined by a similar titration, the loss in active oxygen due to oxidation of the amine was determined to be 0.0066 mole.

The remaining solution in the volumetric flask was transferred to a 250-ml. Erlenmeyer flask, cooled in ice, and a 20% solution of potassium hydroxide was added dropwise, with stirring, until the solution became alkaline to litmus. The viscous oil that separated was removed by extracting the mixture with five 30-ml. portions of ether or chloroform. The extracts were dried over potassium carbonate and concentrated. The viscous residue was treated with picric acid in ethanol, and after recrystallization from aqueous ethanol there was obtained 2.57 g. (93% based on tri-*n*-amylamine) of tri-*n*-amylamine oxide picrate, m.p. 57.8–58.8°.

Thermal Decomposition of Trialkylamine Oxides.—The general procedure followed is illustrated by the pyrolysis of tri-*n*-amylamine oxide.

To a 100-ml. flask fitted with a capillary nitrogen inlet was added the sirupy tri-*n*-amylamine oxide prepared from 23.0 g. (0.101 mole) of tri-*n*-amylamine by oxidation with peracetic acid as described above. The flask was connected to a 25-cm. Vigreux column with an air-cooled condenser which led to three receivers connected in series. The first was cooled with ice, the second with Dry Ice–acetone and the third with liquid nitrogen. The nitrogen atmosphere in the system was evacuated to a pressure of about 20 mm., and the flask was immersed in an oil-bath. The temperature of the bath was raised slowly to 120°. Vigorous boiling occurred at this temperature, followed by distillation of liquid products. The pressure was reduced gradually to 4 mm. and the bath temperature was raised to 160° to complete the decomposition and distillation.

Filtration of the contents of the first receiver yielded 16.3 g. (75%) of crude N,N-di-*n*-amylhydroxylamine, m.p. 54–57°, which after recrystallization from aqueous methanol had m.p. 57–58°.

The liquid contents of the second and third receivers were combined and cooled with Dry Ice to freeze the aqueous layer. The organic layer was removed with a hypodermic syringe and amounted to 4.60 g. (65% based on tri-*n*-amylamine) of 1-pentene. After drying over magnesium sulfate at 5°, the 1-pentene was distilled through a semimicro column; b.p. 28.5–29°, n^{25}D 1.3675 (lit.[12] b.p. 29.97°, n^{25}D 1.3683). The infrared spectrum of the 1-pentene was identical with the spectrum of an authentic sample.[13]

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(9) A. C. Cope, R. A. Pike and C. F. Spencer, THIS JOURNAL, **75**, 3212 (1953).

(10) Obtained from the Becco Sales Corporation, Buffalo, N. Y.

(11) See ref. 5 for the procedure for standardization.

(12) American Petroleum Institute Research Project 44, "Selected Values of Properties of Hydrocarbons," Table 24a.

(13) American Petroleum Institute Research Project 44, "Catalog of Infrared Spectrograms," Serial No. 275 contributed by Universal Oil Products Co.