was removed. The residue was recrystallized from heptane to give 180 mg. (23%) of white **1**, m.p. 150–152° (lit. m.p. 151–152°,[2] 153–154°[1]).

B.—A mixture of 1.50 g. (0.0041 mole) of *p*-toluenesulfonate **2c** and about 0.5 g. of sodium sulfide hydrate in 100 ml. of ethanol was stirred for 15 min. and then about 2.5 g. of sodium sulfide hydrate in 10 ml. of water was added. The mixture was stirred for 1 hr. and refluxed for 0.5 hr. The solvent was removed and the residue was taken up in methylene chloride and extracted with dilute sodium hydroxide and dilute sodium bicarbonate solution. The methylene chloride solution was dried with sodium sulfate and the solvent was removed. The residue was recrystallized from hot heptane to give 410 mg. (58%) of product, m.p. 128–135°, which vapor phase chromatography showed to be 64% **1** and 36% **3**.

C.—Vacuum thermal decomposition (160–170°, 0.02 mm.) of 2.0 g. (0.0066 mole) of **2b** yielded 500 mg. of sublimed material which was dissolved in methylene chloride, filtered through sodium sulfate, and concentrated to dryness to give 500 mg. (43%) of **1**, m.p. 152–153.5°.

In a similar, small-scale experiment, the volatile reaction product was collected and shown to be dimethyl sulfate by mass spectrometry.

Acknowledgment.—The author wishes to thank Miss T. Davis, Mr. G. P. Happ, Mr. D. P. Maier, Dr. T. H. Regan, Dr. J. K. O'Loane, Dr. O. E. Schupp, and Mr. D. S. Cox, for analytical services.

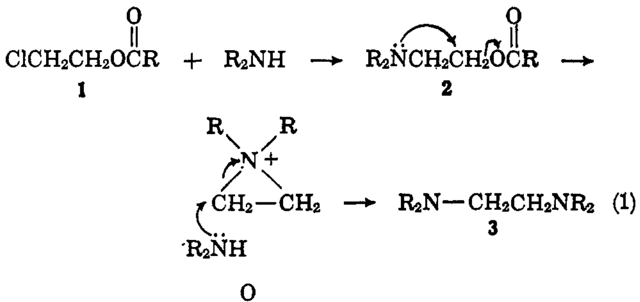
Alkyl Oxygen Cleavage of Esters with Hindered Amines

LESTER WEINTRAUB AND ROSS TERRELL

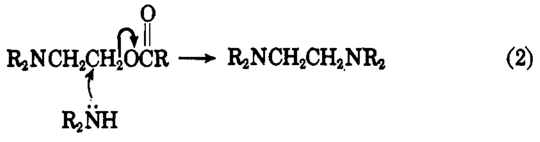
Central Research Laboratories, Air Reduction Company, Inc., Murray Hill, New Jersey

Received October 29, 1964

The bimolecular alkyl oxygen cleavage of a hindered ester by primary and secondary amines has recently been reported.[1] We have found what appears to be another example of alkyl oxygen cleavage[2] in the reaction of hindered secondary amines with 2-chloroethyl carbonates and acetates. The products of this reaction are tetrasubstituted ethylenediamines and are probably formed by a bimolecular reaction with neighboring group participation (eq. 1), although a simple alkyl oxygen cleavage cannot be ruled out (eq. 2).

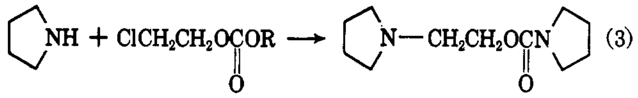


$$\underset{\mathbf{1}}{ClCH_2CH_2OCR} + R_2NH \longrightarrow \underset{\mathbf{2}}{R_2NCH_2CH_2OCR} \longrightarrow [R_2N^+(CH_2CH_2)] + R_2NH \longrightarrow \underset{\mathbf{3}}{R_2N{-}CH_2CH_2NR_2} \quad (1)$$

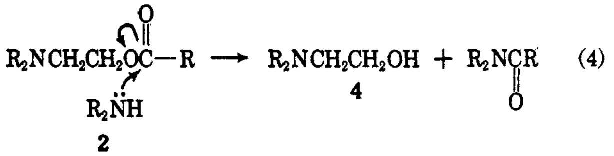


$$R_2NCH_2CH_2OCR \longrightarrow R_2NCH_2CH_2NR_2 \quad (2)$$

The reactions of bis(2-chloroethyl) carbonate, 2-chloroethyl ethyl carbonate, and 2-chloroethyl acetate with hindered amines such as dicyclohexylamine, diisobutylamine, and di(2-ethylhexyl)amine yield the tetrasubstituted ethylenediamines **3** while the reaction with the unhindered amine pyrrolidine yields the product resulting from acyl oxygen cleavage (eq. 3).



The possibility that the amino ester **2** is first cleaved to the amino alcohol **4** which might react further with amines (eq. 4) has been ruled out since, N,N-dicyclohexylaminoethanol does not react with dicyclohexylamine under the same conditions which yield diamine from the amino ester **2**.



$$\underset{\mathbf{2}}{R_2NCH_2CH_2OC{-}R} \longrightarrow \underset{\mathbf{4}}{R_2NCH_2CH_2OH} + R_2NCR \quad (4)$$

Experimental

N,N,N',N'-Tetracyclohexylethylenediamine.—A mixture of dicyclohexylamine (217 g., 1.2 moles) and bis(2-chloroethyl) carbonate (37.4 g., 0.2 mole) was heated at 175° with stirring for 20 hr. The reaction mixture was neutralized with 20% sodium hydroxide, cooled, and filtered. The product was recrystallized from acetone–chloroform to give N,N,N',N'-tetracyclohexylethylenediamine, 46 g., 60% yield, m.p. 104–105° (lit.[3] m.p. 104–105°).

Anal. Calcd. for $C_{26}H_{48}N_2$: C, 80.41; H, 12.37; N, 7.21. Found: C, 80.25; H, 12.45; N, 7.34.

The reaction of dicyclohexylamine (0.9 mole) with 2-chloroethyl ethyl carbonate (0.3 mole) gave 35% of the same diamine and with 0.3 mole of 2-chloroethyl acetate a yield of 14%.

N,N,N',N'-Tetraisobutylethylenediamine.—A mixture of diisobutylamine (307 g., 2.4 moles) and bis(2-chloroethyl) carbonate (75 g., 0.4 mole) was heated at 175° in a rocker bomb for 24 hr. The reaction mixture was neutralized with 20% aqueous sodium hydroxide and the precipitated oil was separated and distilled to yield 68 g. (53%) of N,N,N',N'-tetraisobutylethylenediamine, b.p. 112° (3 mm.).

Anal. Calcd. for $C_{18}H_{40}N_2$: C, 76.05; H, 14.09; N, 9.85. Found: C, 75.90; H, 14.28; N, 9.82.

N,N,N',N'-Tetra(2-ethylhexyl)ethylenediamine.—A mixture of bis(2-chloroethyl) carbonate (32 g., 0.17 mole) and bis(2-ethylhexyl)amine (241 g., 1 mole) was heated at 180° with stirring in a 500-ml., three-necked flask for 35 hr. The reaction mixture was cooled and neutralized with 40% aqueous sodium hydroxide, and the product was extracted into ether. The ether solution was dried over magnesium sulfate and distilled to yield 72 g. (83%) of tetra(2-ethylhexyl)ethylenediamine, b.p. 211–212° (2 mm.).

Anal. Calcd. for $C_{34}H_{72}N_2$: C, 80.31; H, 14.17; N, 5.51. Found: C, 80.45; H, 14.32; N, 5.63.

Reaction of Pyrrolidine with Bis(2-chloroethyl) Carbonate.—Pyrrolidine (128 g., 1.8 moles) was added slowly to bis(2-chloroethyl) carbonate (56.3 g., 0.3 mole). When the exothermic reaction ceased, the reaction mixture was poured into a solution of potassium hydroxide (100 g.) in water (200 ml.). The product was extracted into ether using a continuous extractor. The ether solution was dried and the ether was distilled to give 157 g. of crude products. Fractional distillation gave 17.5 g. (25%) of N-2-hydroxyethylpyrrolidine, b.p. 63–64° (3 mm.), $n^{20}\text{D}$ 1.4730. The picrate was crystallized from methanol, m.p. 87–88°.

---

(1) H. E. Zaugg, P. F. Helgren, and A. D. Schaefer, *J. Org. Chem.*, **28**, 2617 (1963).

(2) See P. D. Bartlett and P. N. Rylander, *J. Am. Chem. Soc.*, **73**, 4273 (1951); J. F. Burnett, M. N. Robinson, and F. C. Pennington, *ibid.*, **72**, 2378 (1950), for the other examples of this type of reaction.

(3) T. M. Laakso and D. D. Reynolds, *ibid.*, **73**, 3518 (1951).

Anal. Calcd. for $C_{12}H_{16}N_4O_8$: C, 42.0; H, 4.65; N, 16.3. Found: C, 42.55; H, 5.03; N, 16.58.

In addition there was distilled 40 g. (80%) of the urethan 2-pyrrolidinoethyl pyrrolidine-1-carboxylate, b.p. 137–42° (3 mm.), $n^{20}D$ 1.4872. This product was identified by its infrared spectrum and by analysis of the picrate, m.p. 119–120°, crystallized from methanol.

Anal. Calcd. for $C_{17}H_{23}N_5O_9$: C, 46.3; H, 5.2; N, 15.8. Found: C, 46.44; H, 5.53; N, 15.7.

A Preparation of Primary Aliphatic Nitramines

LAWRENCE J. WINTERS, DAVID B. LEARN,[1] AND SHANTILAL C. DESAI

Department of Chemistry, Drexel Institute of Technology, Philadelphia, Pennsylvania

Received December 14, 1964

Primary aliphatic nitramines have most frequently been prepared by a four-step procedure: (1) acylation of the alkanamine to form the urethan; (2) nitration of the urethan; (3) ammonolysis of the N-nitrourethan to produce the ammonium salt of the nitramine; and (4) acidification of the salt to obtain the N-nitroalkanamine.[2,3]

TABLE I

ALKALINE NITRATION OF AMINES

Nitramine	Solvent	Reaction temp.	Yield, %	Molar ratio, n-C_4H_9Li–RNH_2–$C_2H_5ONO_2$	B.p., °C. (mm.)
$CH_3N(NO_2)H$	Ether	Addition of reactants at Dry Ice temperature, then stirred at room temperature	35[a]	2:2:1[b,c]	80–85 (10)[d]
	Hexane	Dry Ice	22	2:1:1[b]	
i-$C_3H_7N(NO_2)H$	Hexane[e]	Dry Ice	44	2:1:1	
	Ether–hexane (2:1)	Dry Ice	58	2:1:1	
	Hexane	Dry Ice	40	2:1:1[f]	87–88 (10)[g]
	Hexane	Dry Ice	35	1:1:1[c]	
n-$C_4H_9N(NO_2)H$	Hexane	Dry Ice	49	2:1:1	
	Ether–hexane (2:1)	Dry Ice	30	2:1:1	92 (0.5)[h]
sec-$C_4H_9N(NO_2)H$	Hexane[e]	Dry Ice	43.7	2:1:1	110 (10)[i]
	Hexane	Dry Ice	45	3:1:1	
	Hexane	Steam refluxed	4.0	2:1:1	
	Ether	Addition of reactants at 0°, steam refluxed during stirring	15.5	2:1:1	
t-$C_4H_9N(NO_2)H$	Hexane	Dry Ice	37	2:1:1	
	Hexane	0° during n-C_4H_9Li addition, steam refluxed at other times	14	2:1:1	86–87 (10)[j]
n-$C_{10}H_{21}N(NO_2)H$[k]	Ether–hexane (2:1)	Dry Ice	46[l]	2:1:1	

[a] The aqueous layer was continuously extracted with ether for 20 hr. [b] Phenyllithium in ether was used in place of the n-butyllithium reagent. [c] The reactants were added to the reaction mixture in one step. [d] Lit.[2] b.p. 158° (766.3 mm.). [e] The hexane was distilled over lithium aluminum hydride. [f] The addition of ethyl nitrate was done rapidly. [g] B.p. 90–91° (10 mm.) is reported by M. J. C. A. Simon Thomas [*Rec. trav. chim.*, **9**, 77 (1890)]. [h] Lit.[4] b.p. 68–70° (0.05 mm.). [i] B.p. 106.2–106.7° (15 mm.) is reported by G. N. R. Smart and G. F. Wright [*Can. J. Res.*, **B26**, 290 (1948)]. [j] B.p. 94–95° (16 mm.) and 71° (0.6 mm.) are reported by J. Barrott, I. N. Denton, and A. H. Lamberton [*J. Chem. Soc.*, 1998 (1963)]. [k] Crystallized twice from hexane, m.p. 38–38.8°. *Anal.* Calcd. for $C_{10}H_{22}N_2O_2$: C, 59.37; H, 10.96; N, 13.85. Found: C, 59.62; H, 11.08; N, 14.01. [l] Based on the weight of crude product obtained.

Emmons and Freeman[4] have described an alkaline nitration method for the preparation of alkylnitramines using acetone cyanohydrin nitrate as the nitrating agent and an excess of an alkylamine. It is not possible to nitrate amines with branching on the α-carbon atom using this procedure.

We have devised a method[5] for the direct transformation of primary aliphatic amines[6] to the corresponding nitramines. This procedure involves the irreversible conversion of an amine to its conjugate base by n-butyllithium and subsequent nitration using ethyl nitrate as the nitrating agent. Primary, secondary,

$$RNH_2 \xrightarrow{n\text{-}C_4H_9Li} RNHLi \xrightarrow{C_2H_5ONO_2} RN(NO_2)Li \xrightarrow{H^+} RN(NO_2)H$$

and tertiary carbinylamines can be converted to the corresponding nitramine (*cf.* Table I). There are several advantages to this procedure. First, the preparation can be carried out as a one-step process. In addition, the method uses relatively simple equipment, employs readily available commercial reagents, and gives yields of product which are comparable to those obtained by other preparative routes.[2–4] Using this procedure, one can isolate the primary nitramine without conversion to an insoluble salt or secondary nitramine. The main disadvantage to this approach is that amines bearing functional groups reacting with n-butyllithium do not form nitramines. This procedure appears to complement the method of Emmons and Freeman[4] since it is not possible to convert secondary and tertiary carbinylamines using their approach and ours is limited to amines not having reactive functional groups.[7] It is evident that ethyl nitrate is

---

[1] Undergraduate National Science Foundation research participant, 1963–1964.

[2] A. P. N. Franchimont and E. A. Klobbie, *Rec. trav. chim.*, **7**, 343 (1888).

[3] H. M. Curry and J. P. Mason, *J. Am. Chem. Soc.*, **73**, 5043 (1951).

[4] W. D. Emmons and J. P. Freeman, *ibid.*, **77**, 4387 (1955).

[5] Similar methods are well known for the preparation of aromatic nitramines: W. N. White, *et al.*, *J. Org. Chem.*, **26**, 4124 (1961).

[6] The direct nitration of aliphatic amines has been reported using nitryl fluoride, a corrosive gas, as the nitrating agent: H. C. Mandell, Jr., U. S. Patent 3,071,438 (1962); *Chem. Abstr.*, **59**, 447 (1963).

[7] The authors are grateful to the referee for making these observations.