tion product (1.4 g.), after two recrystallizations from benzene, melted at 228–229°. The malonanilide **8** has not been reported. Infrared absorptions (KBr) appeared at 3.01 (m), 3.37 (m), 5.97 (m), 6.06 (s), 6.26 (s), 6.48 (m), 6.58 (s), 6.69 (s), 6.95 (s), 7.62 (m), 8.00 (m), 13.40 (s), and 14.50 (m) μ.

Anal. Calcd. for $C_{20}H_{22}N_2O_2$ (**8**): C, 74.50; H, 6.88; N, 8.69. Found: C, 74.59; H, 6.69; N, 8.54.

A Novel Thermal Dequaternization of a Benzimidazolium Salt

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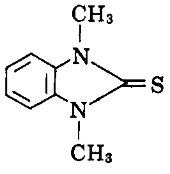
Received February 9, 1965

1,3-Dimethylbenzimidazole-2-thione (**1**) has been prepared from 1,3-dimethyl-2-methylthiobenzimidazolium iodide (**2a**) in refluxing pyridine.[1,2] This reaction may be considered to be a nucleophilic displacement by iodide ion on the methyl group attached to sulfur. In connection with some work on the preparation of various imidazolidine-2-thiones, we have noted that the weakly nucleophilic methosulfate ion can also effect displacement of the methyl group on sulfur of the 1,3-dimethyl-2-methylthiobenzimidazolium cation under certain conditions.[3]



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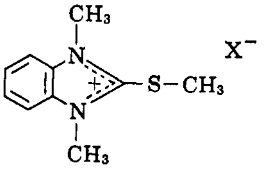

2a, X = I
b, X = CH_3SO_4
c, X = p-$CH_3C_6H_4SO_3$

1,3-Dimethyl-2-methylthiobenzimidazolium methosulfate (**2b**) was obtained by the methylation of 2-benzimidazolethiol in aqueous sodium hydroxide with excess dimethyl sulfate at 6–16°. Other products obtained in this reaction were 1,3-dimethylbenzimidazol-2-one (**3**) and 1-methyl-2-methylthiobenzimidazole (**4**); the latter was converted to 1,3-dimethyl-2-methylthiobenzimidazolium *p*-toluenesulfonate (**2c**) by reaction with methyl *p*-toluenesulfonate. The n.m.r. spectra of **2b** and **2c** confirmed the presence of the common cationic portion of each compound.

The thermal dequaternization of **2b** took place at 160–170° and 0.02 mm. to form **1** and dimethyl sulfate. This reaction was confirmed by an experiment with a mass spectrometer in which a sample of **2b** was decomposed in the heated inlet (230°) and gave a mass spectrum corresponding to a mixture of authentic **1** and dimethyl sulfate. Furthermore, the reversibility of this thermal reaction was shown by the reaction of equimolar amounts of **1** and dimethyl sulfate at 120–145° to give a product which had infrared and n.m.r. spectra identical with those of **2b**.

This thermal dequaternization reaction can be utilized preparatively under conditions of reduced pressure which serve to remove the reaction product, dimethyl sulfate.

Experimental

Methylation of 2-Benzimidazolethiol.—To 1.0 l. of 2 *N* sodium hydroxide at 6° was added 50.0 g. (0.33 mole) of 2-benzimidazolethiol. The solid did not dissolve completely. Dimethyl sulfate (200 g., 1.59 moles) was added slowly (10 min.) while the temperature was maintained between 6 and 16°. The reaction mixture was stirred for 20 min. before methylene chloride was added, with further stirring. The organic layer was separated, dried with sodium sulfate, and concentrated to dryness. A vapor phase chromatographic analysis (F and M Model 720 with SE-30 silicone rubber columns at 210°) of the semisolid residue indicated a 1:1:2 ratio of compounds **3**, **4**, and **2b**. Because of the thermal instability of **2b** in the hot (300°) injection port of the vapor phase chromatograph, the actual product detected was **1** which represented **2b**. The semisolid residue was recrystallized twice from acetone to give 19.5 g. (20%) of **2b**, m.p. 136–137°. Confirmation of structure was had from the following physical and spectral properties. Compound **2b** was soluble in water and had an infrared spectrum (KBr) showing characteristic broad absorptions at 1010 (CH_3–O–S) and 1240 cm.$^{-1}$ (S–O) similar to that for potassium methyl sulfate in addition to aromatic C–C absorption at 1500 cm.$^{-1}$. The n.m.r. spectrum (deuteriochloroform) showed peaks at τ 7.27 (singlet), 6.71 (singlet), 5.81 (singlet), and 2.30 (multiplet) with relative areas of 3, 3, 6, and 4, respectively, and attributable to the S–CH_3, S–O–CH_3, N–CH_3, and aromatic protons, respectively.

Anal. Calcd. for $C_{11}H_{16}N_2O_4S_2$: C, 43.4; H, 5.3; N, 9.2. Found: C, 43.7; H, 5.5; N, 9.1.

The filtrates from isolated **2b** were combined and vacuum distilled to remove nonvolatile material. Upon standing, the distillate deposited crystals (7.3 g.) which were recrystallized from heptane to give 6.0 g. (11%) of **3**, m.p. 107–108° (lit.[4] m.p. 107–108°). The filtrate from which **3** was obtained was separated by preparative vapor phase chromatography (Beckman Megachrom with Apiezon J columns at 210°), and the two components were recrystallized from petroleum ether (b.p. 66–75°) to give 3.5 g. (6%) of **4**, m.p. 55–57° (lit.[1] m.p. 56°), and 1.8 g. (3%) of **3**, m.p. 104–107°.

1,3-Dimethyl-2-methylthiobenzimidazolium *p*-Toluenesulfonate (2c).—To a solution of 1.5 g. (0.0084 mole) of 1-methyl-2-methylthiobenzimidazole in 50 ml. of acetonitrile was added 1.9 g. (0.010 mole) of methyl *p*-toluenesulfonate, and this solution was refluxed for 6 hr. The solvent was removed, leaving an oil which was treated with ether. The crystals which formed weighed 2.84 g. (93%), m.p. 118–125°. The infrared spectrum (KBr) showed characteristic absorption at 1010, 1040, 1125, and 1190–1220 cm.$^{-1}$ for *p*-$CH_3C_6H_4SO_3$, in addition to aromatic absorption at 1490 and 1600 cm.$^{-1}$. The n.m.r. spectrum (deuteriochloroform) showed peaks at τ 7.75 (singlet), 7.34 (singlet), 5.93 (singlet), and 2.55–2.77 (multiplets) with relative areas of 3, 3, 6, and 8, respectively, and attributable to the phenyl CH_3, S–CH_3, N–CH_3, and aromatic protons, respectively.

Anal. Calcd. for $C_{17}H_{20}N_2O_3S_2$: C, 56.0; H, 5.5; N, 7.7. Found: C, 55.8; H, 5.6; N, 7.5.

1,3-Dimethylbenzimidazole-2-thione (1). A.—A mixture of 700 mg. (0.0043 mole) of 1,3-dimethylbenzimidazol-2-one (**3**) and 4.0 g. (0.018 mole) of phosphorus pentasulfide in 100 ml. of *p*-xylene was refluxed for 7 hr. The solution was allowed to cool and was poured into a mixture of methylene chloride and water. The organic layer was removed and dried with sodium sulfate and magnesium sulfate. The solvent was removed and the yellowish residue was treated with hot cyclohexane. The cyclohexane solution was decanted and gave, on cooling, 130 mg. of material, m.p. 148–150°, which was taken up in ether and combined with an ether extract of the cyclohexane-insoluble material. The ether solution was extracted with dilute sodium hydroxide, dilute hydrochloric acid, and sodium bicarbonate solution before it was dried with sodium sulfate and the solvent

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(1) G. F. Duffin and J. D. Kendall, *J. Chem. Soc.*, 361 (1956).

(2) K. Futaki, *J. Pharm. Soc. Japan*, **74**, 1365 (1954).

(3) The nucleophilicity of iodide ion for displacement on carbon is approximately 100 times greater than that of sulfate ion. Presumably the nucleophilicities of sulfate ion and methosulfate ion are similar. See A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 107; J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 161.

(4) J. K. Landquist, *J. Chem. Soc.*, 2830 (1953).

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

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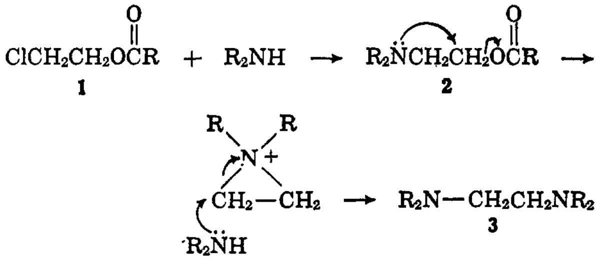
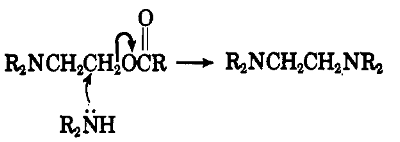
Received October 29, 1964

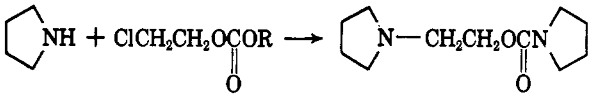
The bimolecular alkyl oxygen cleavage of a hindered ester by primary and secondary amines has recently been reported.[1] We have found what appears to be another example of alkyl oxygen cleavage[2] in the reaction of hindered secondary amines with 2-chloroethyl carbonates and acetates. The products of 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).


(1)

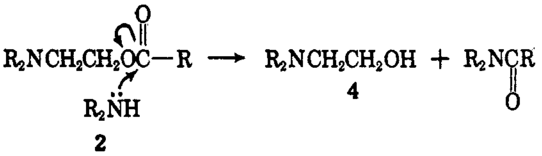


$$\underset{R_2\ddot{N}H}{R_2NCH_2CH_2}O\overset{O}{\overset{\|}{C}}R \longrightarrow R_2NCH_2CH_2NR_2 \qquad (2)$$

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).


(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**.



$$\underset{\underset{\mathbf{2}}{R_2\ddot{N}H}}{R_2NCH_2CH_2}O\overset{O}{\overset{\|}{C}}—R \longrightarrow \underset{\mathbf{4}}{R_2NCH_2CH_2OH} + R_2N\underset{O}{\underset{\|}{C}}R \qquad (4)$$

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.), $n^{20}D$ 1.4730. The picrate was crystallized from methanol, m.p. 87–88°.

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(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).