A mixed melting point with the hydrochloride of morpholinylacetonitrile was 135-140°; a mixed melting point with the hydrochloride of the following compound was 173°. The yield was quantitative. *Anal.* Calcd. for $C_8H_{16}O_3NCl$: N, 6.68. Found: N, 6.69.

Ethyl α-(4-Morpholinyl)-acetate.—A solution of 5.5 g. of ethyl bromoacetate and 5.5 g. of morpholine in 20 ml. of benzene was refluxed for thirty minutes. After the solution was cold, 5.4 g. of morpholine hydrobromide (representing a 98% conversion) was removed by filtration, and the filtrate fractionated. The boiling point of the colorless ester was 227-228° at 767 mm. *Anal.* Calcd. for $C_8H_{15}O_3N$: N, 8.09. Found: N, 8.00.

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UNIVERSITY OF WASHINGTON
SEATTLE 5, WASHINGTON
RONALD A. HENRY
WILLIAM M. DEHN

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Miscellaneous Derivatives of Morpholine

Diphenylcarbamyl Morpholide.—One-hundredth molar quantities of diphenylcarbamyl chloride and morpholine were mixed without benefit of dilution. When the mixture was cold, 20 ml. of water and 1.0 g. of sodium bicarbonate were added and the solution heated to boiling. The precipitated morpholide was removed by filtration and recrystallized twice from ethyl alcohol; large monoclinic prisms, m. p. 110-111°.[1] *Anal.* Calcd. for $C_{17}H_{13}O_2N_2$: N, 9.92. Found: N, 9.82.

Morpholine with Isothiocyanates.—The following thioureas were prepared by heating equivalent quantities of morpholine and the indicated isothiocyanate, and recrystallizing the product from aqueous ethyl alcohol or acetone.

TABLE I

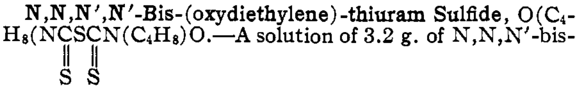
RNCS (R =)	Formula of derivative	M. p. of derivative, °C.	N Analyses, % Calcd.	Found
Phenyl	$C_{11}H_{14}ON_2S$	130.5	12.60	12.62
o-Tolyl	$C_{12}H_{16}ON_2S$	144.5–145.5	11.86	11.79
p-Tolyl	$C_{12}H_{16}ON_2S$	151–151.5	11.86	11.84
Allyl	$C_8H_{14}ON_2S$	56–57	15.04	15.03

4-(Picryl)-morpholine.—To a hot solution of 5.0 g. of picryl chloride in 20 ml. of ethyl alcohol was added 3.4 g. of morpholine in 10 ml. of alcohol. The solution was refluxed for thirty minutes, then poured into 50 ml. of water. The precipitate was removed by filtration and washed carefully with water. The yield was 5.4 g., or 90%; m. p. 160-161°. Recrystallization from ethyl alcohol gave orange-yellow needles exhibiting two melting points. If heated rapidly, the compound melted at 147.5-148.5°, then resolidified and melted a second time at 166-166.5°. If heated slowly only the second melting point was observed. *Anal.* Calcd. for $C_{10}H_{10}O_7N_4$: N, 18.79. Found: N, 18.45.

4-(Picramyl)-morpholine.—This compound was prepared by the reduction of 4-(picryl)-morpholine with hydrogen sulfide in ammoniacal ethyl alcohol; dark red, fern-like crystals from 95% ethyl alcohol, decomposing at 256°. *Anal.* Calcd. for $C_{10}H_{12}O_5N_3$: N, 20.89. Found: N, 20.80.

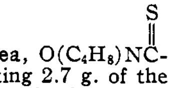
(4-Morpholinyl)-thiocarbonic Acid Amide.—A solution of 2.1 g. of morpholine hydrochloride, 1.6 g. of potassium thiocyanate, and 10 ml. of water was evaporated to dryness on the water-bath. The amide was separated from the potassium chloride by extraction with absolute ethyl alcohol; partial evaporation of the alcohol and cooling gave needles, which melted at 111.5-112.5° after a second crystallization from absolute alcohol.

Anal. Calcd. for $C_5H_{10}ON_2S$: N, 19.2. Found: N, 19.3.



$O(C_4H_8(N\overset{\|}{\underset{S}{C}}S\overset{\|}{\underset{S}{C}}N(C_4H_8)O$

N,N,N',N'-Bis-(oxydiethylene)-thiuram Sulfide, $O(C_4H_8(NCSCN(C_4H_8)O$.—A solution of 3.2 g. of N,N,N'-bis-oxydiethylene thiuram disulfide,[2] 0.7 g. of potassium cyanide, 40 ml. of 95% ethyl alcohol, and 10 ml. of water was refluxed for thirty minutes. The precipitate that formed when 50 ml. of water was added was removed by filtration and washed with water. One recrystallization from alcohol gave bright yellow prismatic needles; m. p. 126-126.5°. *Anal.* Calcd. for $C_{10}H_{16}O_2N_2S_3$: N, 9.21. Found: N, 9.21.



$O(C_4H_8)N\overset{\overset{S}{\|}}{C}N(C_4H_8)O$

N,N,N',N'-Bis-(oxydiethylene)-thiourea, $O(C_4H_8)NCN(C_4H_8)O$.—The melt obtained by heating 2.7 g. of the thiuram disulfide[2] with 1.5 g. of morpholine for four hours at 120° was extracted with 10 ml. of water. The residue consisted of sulfur. The filtrate upon partial evaporation yielded a compound melting at 85 to 90°; two recrystallizations from water gave colorless, hexagonal plates of the monohydrate; m. p. 89.5-90°. *Anal.* Calcd. for $C_9H_{18}O_3N_2S$: N, 11.93. Found: N, 11.92, 11.94.

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[1] All melting points are corrected.

[2] Prepared by Schupe, *J. Assoc. Off. Agr. Chem.*, **23**, 824 (1940), by the action of potassium ferricyanide on morpholinium (4-morpholinyl)-dithiocarbamate.

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UNIVERSITY OF WASHINGTON
SEATTLE 5, WASHINGTON
RONALD A. HENRY
WILLIAM M. DEHN

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Some Derivatives of the 3- and 5-Nitro-2-aminopicolines[1]

In connection with our work on the cyclization of 2-aminopyridine derivatives it became of interest to prepare the following compounds derived from the 3- and 5-nitro-2-aminopicolines.

3- and 5-Nitro-2-aminopicolines.—These were prepared by the nitration of the 2-aminopicolines. All except 3-nitro-2-amino-5-methylpyridine have been previously reported.[2,3,4] This compound was prepared by the nitration of 10 g. (0.093 mole) of 2-amino-5-methylpyridine at 0° in sulfuric acid following the method of Seide.[3] The yield of pale yellow crystals was 8.5 g. (60%), m. p. after recrystallization from water, 190-191°. *Anal.*[5] Calcd. for $C_6H_7O_2N_3$: N, 27.45. Found: N, 27.38.

2,3-Diaminopicolines.—These were prepared by low pressure catalytic hydrogenation of the corresponding 3-nitro-2-aminopicolines in ethanol solution using a palladium-on-charcoal catalyst. In each case the reaction required twenty-four hours for completion when 7.7 g. (0.05 mole) of the starting material was used. The products were purified by recrystallization from benzene-hexane mixture. The purified diaminopicolines darkened rapidly on exposure to air and eventually became tars. When this procedure was applied to the 5-nitro-2-aminopicolines only tars could be isolated from the hydrogenation.

2,3-Diamino-4-methylpyridine.—Yield 4.3 g. (70%), m. p. 115-116°. *Anal.*[5] Calcd. for $C_6H_9N_3$: N, 34.15. Found: N, 34.06.

2,3-Diamino-5-methylpyridine.—Yield 2.0 g. (32%), m. p. 85-86°. *Anal.*[5] Calcd. for $C_6H_9N_3$: N, 34.15. Found: N, 34.24.

2,3-Diamino-6-methylpyridine.—Yield 3.6 g. (54%), m. p. 69-70°. *Anal.*[5] Calcd. for $C_6H_9N_3$: N, 34.15. Found: N, 34.00.

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[1] The work described in this paper was carried out under a Frederick Gardner Cottrell Special Grant-in-Aid from the Research Corporation.

[2] Seide, *Ber.*, **57**, 791 (1924).

[3] Seide, *ibid.*, **57**, 1802 (1924).

[4] Seide, *J. Russ. Phys.-Chem. Soc.*, **50**, 534 (1924).

[5] Microanalysis by the Clark Microanalytical Laboratory, Urbana, Ill.