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A Synthesis of Amine Salts of Thiocyanic Acid

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Amine salts of thiocyanic acid have been prepared by the reaction of amines with thiocyanogen[2,3] and by the reaction of benzylamine hydrochloride with potassium thiocyanate.[4] Isolation of the product by these methods was troublesome and rather low yields were obtained.

The reaction of ammonium thiocyanate with amines[5] to form these compounds apparently has attracted little investigation. When ammonium thiocyanate is heated with primary and secondary alkyl, alicyclic or heterocyclic amines, ammonia is quantitatively evolved and amine salts of thiocyanic acid are formed. By means of this synthesis, amine salts of thiocyanic acid can be prepared by a simple procedure and the products can be readily isolated in high yields.

The compounds described are colorless, crystalline, stable solids or mobile liquids. They give positive tests for the thiocyanate ion with silver nitrate and with ferric chloride and liberate amine when heated in the presence of sodium hydroxide.

Experimental[6]

The general procedure of preparation is illustrated by the following example.

Isopropylammonium Thiocyanate.—Seventy-six grams (1 mole) of ammonium thiocyanate was added to 88 g. (1 mole) of a 67% water solution of isopropylamine. This solution was heated at 85–90° until the evolution of ammonia had ceased (about one hour) and was then held at 50° until the removal of water was complete. When cooled, the colorless, crystalline mass was extracted with benzene, filtered and dried to give 103 g. (87% yield) of product melting at 68–70°. After recrystallizing from ethanol, the melting point was 85–86°.

Anal. Calcd. for $C_4H_{10}N_2S$: C, 40.68; H, 8.48; N, 23.72; S, 27.12; mol. wt., 118. Found: C, 40.56; H, 8.58; N, 23.62; S, 27.22; mol. wt., 120.

A sample prepared by Lecher's method,[2] after recrystallization from methanol, melted at 82–83°. The melting point of the mixture was unchanged. The isomeric 1-isopropyl-2-thiourea was prepared by treating isopropyl isothiocyanate with isopropylamine. This compound melted at 168–169°.

Isopropylammonium thiocyanate (crude product) was more definitely characterized by an argentometric determination of the thiocyanate ion, a purity of 98.1% being shown by this analysis. The isopropylamine volatilized by boiling a sample with sodium hydroxide was collected and a volumetric analysis showed a purity of 97.7%.

TABLE I

AMINE SALTS OF THIOCYANIC ACID—RNH_3SCN AND R_2NH_2SCN

R	B. p.[a] or m. p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found	Mol. wt. Calcd.	Mol. wt. Found
n-Butyl[b]		$C_5H_{12}N_2S$					21.20	21.36	24.26	24.41		
Di-*n*-butyl[c]	130–131	$C_9H_{20}N_2S$	57.44	57.10	10.64	10.74	14.89	14.91	17.03	16.99		
Di-*n*-propyl[d]	159–161	$C_7H_{16}N_2S$	52.50	52.47	10.00	9.95	17.50	17.60	20.00	19.98		
2-Aminoethyl[e]	28–30	$C_3H_9N_3S$					35.27	35.36	26.90	27.00		
Cyclopentamethylene[f]	93–94	$C_6H_{12}N_2S$	49.96	49.91	8.38	8.37	19.43	19.53	22.23	22.26		
Cyclohexyl[g]	93–94	$C_7H_{14}N_2S$	53.12	53.08	8.92	8.83	17.70	17.82	20.26	20.35	158	160
Dicyclohexyl[h]	238	$C_{13}H_{24}N_2S$	65.00	64.95	10.00	10.08	11.67	11.70	13.33	13.19	240	249
1-Oxa-2,3,5,6-tetramethylene[i]	149	$C_5H_{10}N_2OS$	41.07	41.05	6.89	6.83	19.17	19.17	21.93	22.02	146	154
Benzyl[j]	99–100	$C_8H_{10}N_2S$	57.79	57.77	6.07	6.07	16.85	16.87	19.29	19.40	166	160
Dibenzyl[k]	158–159	$C_{15}H_{16}N_2S$	70.27	70.10	6.29	6.23	10.93	10.97	12.51	12.60	256	261

[a] All melting points and boiling points are uncorrected. [b] Purification was effected by heating under reduced pressure and analyzing the residue; n^{20}_D 1.5173. [c] Distilled at 0.2 mm.; n^{20}_D 1.4975. [d] Distilled at 0.4 mm.; n^{20}_D 1.5102. [e] Recrystallized from alcohol. [f,g,h] Recrystallized from chloroform. [i] This compound is derived from morpholine. [j] Melting points reported: (3) 100–101°; (4) 101–102°. [k] Recrystallized from water.

Fifteen per cent. of the product was converted to 1-isopropyl-2-thiourea when refluxed in ethylbenzene for eighteen hours.

Summary

A synthesis of amine salts of thiocyanic acid, which is effected by the reaction of ammonium thiocyanate with primary or secondary amines, is described. The preparation by this method of 10 new compounds is reported.

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[1] Present address: Marathon Corporation, Rothschild, Wis.

[2] Lecher, Wittwer and Speer, *Ber.*, **56**, 104 (1923).

[3] Jones and Fleck, THIS JOURNAL, **50**, 2018 (1928).

[4] Dixon, *J. Chem. Soc.*, **59**, 553 (1891).

[5] Dietrich, U. S. Patent 2,362,890.

[6] The melting points given are uncorrected.