

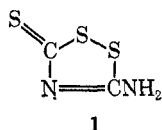
The Basicity of Isoperthiocyanic Acid

RAYMOND SELTZER¹ AND WILLIAM J. CONSIDINE¹

M & T Chemicals Inc., Subsidiary of American Can Company, Corporate Research Laboratories, Rahway, New Jersey 07065

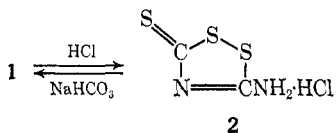
Received February 11, 1969

Isoperthiocyanic acid, or 3-amino-5-thione-1,2,4-dithiazole (1), was first isolated by Wöhler,² but its



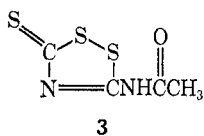
structure was proven only recently.^{3,4} The literature⁵ contains many examples illustrating the "acid" character of 1; it reacts with amines and hydroxide ion to give ring-opening products. However, there is only one questionable example^{6,7} relating to the expected basic properties of 1. In this note, we provide evidence for the basicity of 1 *via* reactions at the exocyclic amino group.

The addition of gaseous HCl to a solution of isoperthiocyanic acid (1) in acetonitrile gave the hydrochloride (2) in 46% yield. Compound 1 can be recovered in



80% yield by adding 2 to aqueous sodium bicarbonate. Attempts to dissolve 2 for recrystallization or nmr measurements led to 1. However, the ir spectrum showed broad multiple NH absorption at 3200–3090 cm^{-1} and a strong NH deformation frequency at 1615 cm^{-1} , characteristic of primary amine hydrochlorides.⁸

An acetyl derivative of 1 was reported,^{6,7} but its structure was not proven. We have treated 1 with acetic anhydride, and isolated a compound to which we assign structure 3. Acid hydrolysis of 3 regenerated 1



in 71% yield. The nmr spectrum (acetone- d_6) of 3 showed methyl and NH proton absorptions, in the correct ratio, at 2.41 and 3.62 ppm, respectively. The ir spectrum showed the amide I band at 1695 cm^{-1} , NH stretching frequency for secondary amides at 3110 and 3220 cm^{-1} ,⁸ an amide II band at 1510 cm^{-1} ,⁹ and imine absorption at 1500 cm^{-1} .¹⁰

(1) Geigy Chemical Co., Ardsley, N. Y. 10502.

(2) A. Wöhler, *Ann. Phys.*, **69**, 273 (1821).

(3) A. Hordvik, *Acta Chem. Scand.*, **15**, 1186 (1961).

(4) H. J. Emeléus, A. Haas, and N. J. Shepperd, *J. Chem. Soc.*, 3165 (1963).

(5) L. L. Bambas, "The Chemistry of Heterocyclic Compounds," Vol. 4, Interscience Publishers, New York, N. Y., 1952, p 35.

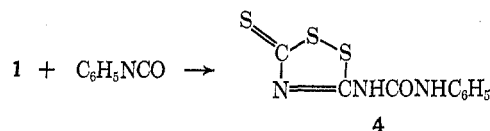
(6) M. P. de Clermont, *Bull. Soc. Chim. Fr.*, **25**(2), 525 (1876).

(7) A. Hantzsch and M. Wolvekamp, *Ann. Chem.*, **331**, 265 (1904).

(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1960, pp 249, 259.

The acetyl derivative (3) is soluble in 6 *N* aqueous ammonia and can be recovered unchanged on acidification with aqueous hydrochloric acid. However, we have confirmed Hantzsch's observation that 3 undergoes a ring-opening reaction with 10% aqueous sodium hydroxide; sulfur was isolated. Isoperthiocyanic acid (1) undergoes ring-opening reactions with hydroxide ion and ammonia. Thus hydrolysis of the amide linkage is undoubtedly required for the opening of the dithiazole ring in 3.

A urea derivative (4) of isoperthiocyanic acid was prepared in 53% yield by allowing a mixture of 1 and phenyl isocyanate to react in refluxing dioxane. At-



tempts to hydrolyze 4 to 1 led to decomposition of the dithiazole ring. Sulfur was the only product isolated. This result is not surprising in view of the vigorous conditions required for the hydrolysis of a urea linkage. The infrared spectrum of 4 is consistent with the assigned structure; it showed broad NH stretching absorption in the 3120–3000- cm^{-1} region and carbonyl absorption at 1680 cm^{-1} . The nmr spectrum (dimethyl sulfoxide- d_6) shows multiple absorption at 7.10–7.60 ppm, characteristic of the phenyl protons, and additional absorption at 8.10 and 9.50 ppm, consistent with the two amide protons. The absorptions were in the appropriate ratio.

In contrast to the amide derivative 3, the urea derivative 4 can be recovered unchanged from 10% aqueous sodium hydroxide solution, demonstrating the stability of the urea linkage. Thus we have additional evidence that substitution at the exocyclic amino group in isoperthiocyanic acid stabilizes the dithiazole nucleus to ring-opening reactions.

Experimental Section

The infrared spectra were determined on a Beckman IR-8 spectrophotometer in Nujol and Fluorolube. The nmr spectra were determined on a Varian A-60 spectrometer using tetramethylsilane as the internal standard. The spectrum of 4 was determined at 70° for solubility reasons.

Isoperthiocyanic Acid (1).—Klason's¹¹ procedure was used to prepare 1. To a solution of 1000.0 g (13.2 mol) of ammonium thiocyanate in 400 ml of water was added dropwise 1000 ml (11.8 mol) of 36% hydrochloric acid. A solid deposited during the addition which turned yellow on standing. Gas evolution was observed after the addition was complete, and the reaction mixture was allowed to stand at room temperature for 3 days. The latter step was taken as a precaution, as hydrogen cyanide is liberated in the reaction. The reaction mixture was filtered, and the residue was washed with water until chloride free. Air drying gave 317.0 g (54%), mp 200° dec. Recrystallization from a dimethyl sulfoxide–water solution gave an analytical sample, mp 202° dec.

Anal. Calcd for $\text{C}_2\text{H}_2\text{N}_2\text{S}_3$: N, 18.6; S, 64.0. Found: N, 18.3; S, 63.9.

3-Acetamido-5-thione-1,2,4-dithiazole (3).—A mixture of 150.0 g (1.0 mol) of isoperthiocyanic acid and 1500 ml of acetic anhydride was heated with stirring at 110° for 2 hr. After cooling, the mixture was filtered and the residue was washed with methanol and dried to give 141.0 g (73%) of a yellow solid, mp 211–

(9) Reference 8, pp 205–208.

(10) Emeléus assigned the band at 1515 cm^{-1} in 1 to the imine linkage.

(11) P. Klason, *J. Prakt. Chem.*, **38** (2), 366 (1883).

213° dec. Recrystallization of a sample from acetonitrile gave pure **3**, mp 212–213° dec.

Anal. Calcd for $C_4H_4N_2OS_3$: N, 14.6; S, 49.9. Found: N, 14.6; S, 49.4.

Hydrolysis of 3.—A mixture of 4.5 g (0.023 mol) of **3**, 10 ml of concentrated HCl, and 20 ml of ethanol was heated to the reflux temperature. The mixture turned homogeneous, but solids deposited on continued reaction at the reflux temperature. After heating for 2.5 hr, the mixture was cooled and filtered. The residue was washed chloride free with water and dried, yield 2.5 g, mp 200° dec. A mixture melting point with an analytical sample of **1** was not depressed. The ir spectrum was identical with that of **1**. Therefore, a 71% yield of isopertthiocyanic acid was recovered.

3-Amino-5-thione-1,2,4-dithiazole Hydrochloride (2).—A mixture of 20.0 g of isopertthiocyanic acid (**1**) and 2 l. of acetonitrile was refluxed for 2 hr and allowed to cool overnight. The mixture was filtered; 5.3 g (0.035 mol) of **1** remained in solution. To the solution, at room temperature, was added HCl gas for 40 min. Solids precipitated which were filtered, washed with acetonitrile, and dried, yield of **2** 3.0 g (46%), mp 190° dec. Attempts to recrystallize **2** regenerated **1**.

Anal. Calcd for $C_2H_3ClN_2S_3$: Cl, 18.9; N, 15.0; S, 51.5. Found: Cl, 18.4; N, 15.2; S, 51.0.

To a solution of 0.08 g (0.01 mol) of sodium bicarbonate in 10 ml of water was added in small portions 0.18 g (0.01 mol) of **2**. Immediate gas evolution occurred, and the mixture was stirred at room temperature for 30 min. The mixture was filtered, and the residue was washed with water and then air-dried to give 0.12 g (80%) of **1**, mp 200° dec. A mixture melting point with an analytical sample of **1** was not depressed. The ir spectra of the two samples of **1** were identical.

N-Phenyl-N'-(5-thione-1,2,4-dithiazyl-3)urea (4).—A mixture of 75.0 g (0.50 mol) of **1** and 59.5 g (0.50 mol) of phenyl isocyanate in 3 l. of dioxane was refluxed for 3.5 hr. After cooling, the mixture was filtered, and the residue was washed with dioxane until the filtrate was colorless. Drying the product at 100° under vacuum gave 105.0 g of a yellow solid, mp 227–229° dec. Recrystallization from dimethylformamide followed by washing the product with ethyl ether gave 61.0 g (45%) of pure **4**, mp 220–221° dec.¹² An additional recrystallization did not change the melting point. Cooling the mother liquor gave an additional 10.0 g (8%) of pure **4**, mp 220–221° dec.

Anal. Calcd for $C_9H_7N_3OS_2$: C, 40.2; H, 2.6; N, 15.6; S, 35.7. Found: C, 40.3; H, 2.7; N, 15.7; S, 35.2.

Registry No.—**1**, 14453-29-3; **2**, 23405-39-2; **3**, 23405-40-5; **4**, 23405-41-6.

Acknowledgment.—The authors are grateful to Mr. Patrick Branigan, Mr. Ivor Simmons, and their staffs for the elemental and spectral analyses, respectively.

(12) The higher melting point of the crude product is undoubtedly due to the presence of unreacted isopertthiocyanic acid (**1**). Compound **1** melts with decomposition at 202°.

Studies of Organoindium Compounds. The Reaction of Triethylindium with an Excess of Phenyl Isocyanate

HISASHI TADA AND ROKURO OKAWARA

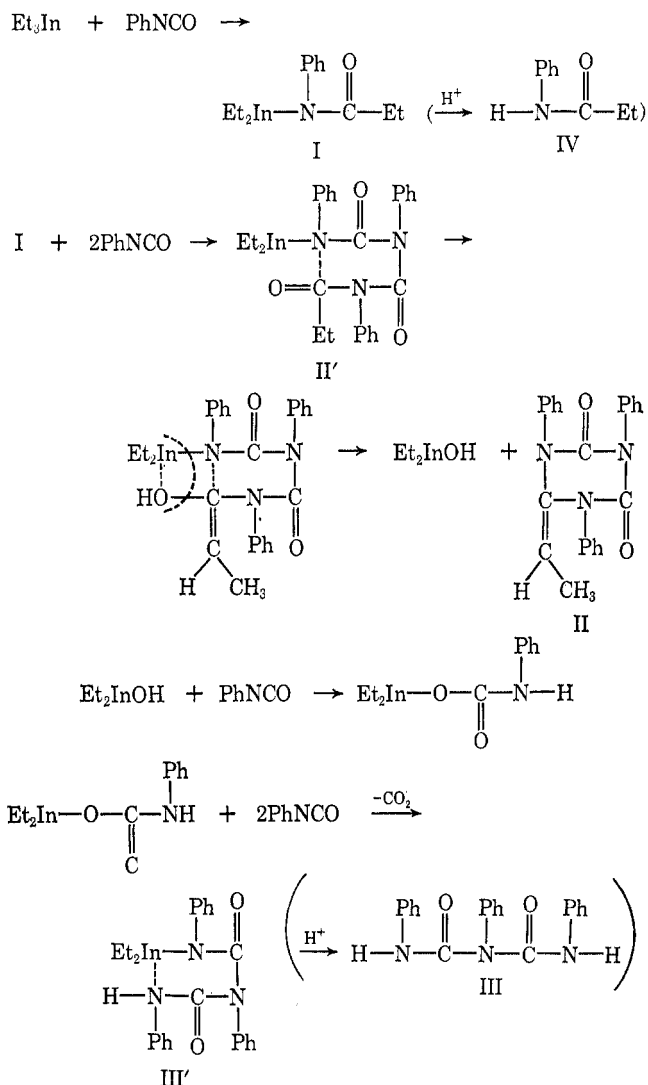
Department of Applied Chemistry, Osaka University,
Yamadakami, Suita, Osaka, Japan

Received July 29, 1969

In a previous paper, we reported the reaction of triethylindium with an equimolar amount of phenyl isocyanate to give N-diethylindium-N-phenylpropionamide (**I**, 89%) and a small amount of unknown compounds.¹

In this paper we describe the reaction of triethylindium with an excess of phenyl isocyanate to give 2,4-dioxo-6-ethylidene-1,3,5-triphenylhexahydro-1,3,5-triazine (**II**), N,N',N''-triphenylbiuret (**III**), N-phenylpropionamide (**IV**), and 2,4-dioxo-6,6-diethyl-1,3,5-triphenylhexahydro-1,3,5-triazine (**V**). Although many organometallic compounds have been known to catalyze the trimerization of isocyanates,² the type of reaction described here has never been observed for other organometallic compounds. The results are shown in Table I and the probable reaction scheme is presented below (Scheme I).

SCHEME I



In the reaction of triethylindium and phenyl isocyanate in a 1:3 molar ratio, the yields of **II** and **III** were low and that of **IV** was moderate, but, in the case of a 1:6.3 molar ratio, the yields of **II** and **III** increased and that of **IV** decreased remarkably. These changes in the yield of products with different molar ratios can be reasonably explained by assuming that **I** is formed at first and is then consumed by the successive insertion of

(1) H. Tada, K. Yasuda, and R. Okawara, *J. Organometal. Chem.*, **16**, 215 (1969).

(2) (a) A. J. Bloodworth and A. G. Davies, *J. Chem. Soc.*, 6858 (1965); (b) S. Herbstman, *J. Org. Chem.*, **30**, 1259 (1965); (c) J. G. Noltes and J. Boersma, *J. Organometal. Chem.*, **7**, P6 (1967).