Preparative vpc[34] provided a sample of pure **13** which had spectral properties identical with the sample obtained from *trans*-1-decalone. The semicarbazone, mp 207–208°, showed no depression on mixture melting point determination with the semicarbazone prepared above.

Ketone **14** was collected by preparative vpc and exhibited infrared absorption[35] at 1702 cm^{-1} (C=O) and nmr absorption at δ 2.31–2.48 (4 H, multiplet, $-CH_2C(=O)CH_2-$) with unresolved absorption in region 0.90–1.90 (14 H).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.39; H, 11.01.

The semicarbazone was prepared and after recrystallization from aqueous alcohol had mp 212–213.5°.

Ring Expansion of Amino Alcohol 11.—Using the same procedure as for the ring expansion of amino alcohol **10**, 0.100 g of **11** afforded 0.060 g of crude product which was composed of 5% epoxide **7**, 45% ketone **13**, 48% ketone **14**, and 2% unidentified products. In another run 0.064 of crude product was obtained which consisted of 0.5% **7**, 48% **13**, 48% **14**, and 4% unidentified products.

Ring Expansion of *trans*-2-Decalone (12) with Diazomethane.—To a solution of 1.00 g (6.5 mmol) of **12** in 20 ml of 3% methanolic potassium carbonate solution at 0° was added a solution of 0.068 g (0.65 mmol) of N-nitroso-N-methylurea in 5 ml of methanol over a 10-min period. The reaction mixture was stirred at room temperature for 12 hr and the methanol removed under reduced pressure. Work-up in the usual manner afforded 1.00 g of crude product. Analysis by vpc[34] indicated the presence of 91% unreacted **12**, 0.4% epoxide **6**, 0.1% epoxide **7**, 3.8% ketone **13**, and 4.8% ketone **14**. Ketones **13** and **14** were collected and had spectral properties identical with those of previously obtained samples.

Registry No.—**8**, 16021-09-3; **9**, 16033-87-7; **10**, 16021-04-8; **11**, 16021-05-9; **12**, 16021-08-2; **14**, 16021-06-0; **14**, semicarbazone, 16021-07-1.

---

[35] Determined as a solution in carbon disulfide.

The Reactions of Carbamoyl Chlorides with Thiocyanate Ion

LANGLEY A. SPURLOCK AND PETER E. NEWALLIS

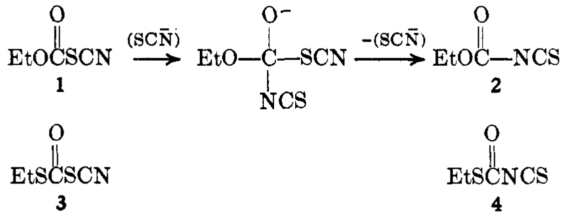
Department of Chemistry, Temple University of the Commonwealth System of Higher Education, Philadelphia, Pennsylvania, and General Chemical Division, Allied Chemical Corporation, Morristown, New Jersey

Received July 7, 1967

Diphenylcarbamoyl thiocyanate (**6**) and dimethylcarbamoyl isothiocyanate (**9**) were prepared by reaction of the corresponding carbamoyl chlorides with potassium thiocyanate in acetonitrile. Dimethylcarbamoyl thiocyanate (**17**) could only be prepared by an indirect method. Thiocyanates **6** and **17** were found to isomerize to their respective isothiocyanates **7** and **9** at drastically different rates (**17** ≫ **6**). Some mechanistic implications of these results are discussed in relation to other acyl thiocyanate isomerizations.

In the course of our investigations of thiocyanate isomerizations, we became interested in the preparation of certain dialkyl- and diarylcarbamoyl thiocyanates.

Previous reports,[1] and our own observations, indicated that the reaction of an acyl chloride with thiocyanate ion produces, with a few exceptions, exclusively the acyl isothiocyanate. These exceptions led us to believe that the stability of acyl thiocyanates may be related to the facility of nucleophilic attack by thiocyanate ion on the acyl carbon. The mode of isomerization is assumed to be a simple addition–elimination sequence (illustrated by the conversion of **1** into **2**). Lending support to this theory is the report that ethoxycarbonyl thiocyanate (**1**) can be isolated [and isomerized to ethoxycarbonyl isothiocyanate (**2**) in the presence of additional thiocyanate ion] while ethylthiocarbonyl isothiocyanate (**4**) is the only isolable product from its similar preparation.[2] It is probable that the stability of **1** is the result of electronic overlap by the ether oxygen with the adjacent carbonyl π system. This could reduce nucleophilic attack on the acyl carbon, rendering **1** isolable. By contrast, the adjacent sulfur of the thio analog, **3**, cannot provide overlap of a similar magnitude,[3] and so any intermediate thiocyanate would be subject to rapid attack by thiocyanate ion giving the isomerized product, **4**.

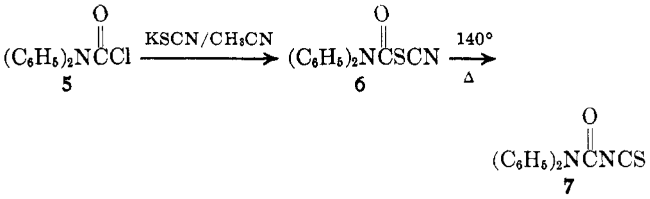


$$\underset{\mathbf{1}}{\mathrm{EtO\overset{O}{\overset{\|}{C}}SCN}} \xrightarrow{(\mathrm{SC\bar{N}})} \mathrm{EtO{-}\overset{O^-}{\overset{|}{C}}{-}SCN} \xrightarrow{-(\mathrm{SC\bar{N}})} \underset{\mathbf{2}}{\mathrm{EtO\overset{O}{\overset{\|}{C}}{-}NCS}}$$

with NCS on the central carbon of the intermediate.

$$\underset{\mathbf{3}}{\mathrm{EtS\overset{O}{\overset{\|}{C}}SCN}} \qquad \underset{\mathbf{4}}{\mathrm{EtS\overset{O}{\overset{\|}{C}}NCS}}$$

Because of the probability that a nitrogen atom, in contrast to sulfur, could provide better electronic overlap than an oxygen atom with the carbonyl π system, it seemed likely that the carbamoyl derivatives would provide an adequate test for this theory. One compound of this type, diphenylcarbamoyl thiocyanate (**6**), had been previously reported[4] when our investigation was initiated. A reinvestigation of its preparation was undertaken.



$$\underset{\mathbf{5}}{\mathrm{(C_6H_5)_2N\overset{O}{\overset{\|}{C}}Cl}} \xrightarrow{\mathrm{KSCN/CH_3CN}} \underset{\mathbf{6}}{\mathrm{(C_6H_5)_2N\overset{O}{\overset{\|}{C}}SCN}} \xrightarrow[\Delta]{140^\circ} \underset{\mathbf{7}}{\mathrm{(C_6H_5)_2N\overset{O}{\overset{\|}{C}}NCS}}$$

From the reaction of diphenylcarbamoyl chloride (**5**) with potassium thiocyanate was obtained a crystalline solid, which could be identified as **6** on the basis of elemental analysis and infrared absorption at 2160 (–SCN) and 1725 cm^{-1} (C=O). The employment of acetonitrile as solvent for this reaction resulted in substantially better yields of **6** (35%) than with ethanol

---

[1] A. E. Dixon and J. Taylor, *J. Chem. Soc.*, **93**, 684 (1908); J. C. Ambeland and T. B. Johnson, *J. Amer. Chem. Soc.*, **61**, 632 (1939); I. B. Douglass and F. B. Dains, *ibid.*, **56**, 719, 1408 (1934); R. H. Patton and J. H. Simens, *ibid.*, **77**, 2017 (1955); D. T. Elmore and J. R. Ogle, *Tetrahedron*, **3**, 310 (1958); W. Ruske and M. Keilert, *Ber.*, **94**, 2695 (1961).

[2] A. Takamizawa, K. Hirai, and K. Matsui, *Bull. Chem. Soc. Jap.*, **36**, 1214 (1963).

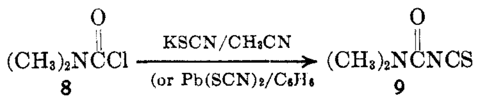
[3] The analogous positive mesomeric effect of the CH_3S- group has been shown to be roughly half that of the CH_3O- group. See H. Lumbroso and C. Marschalk, *J. Chim. Phys.*, **49**, 385 (1952); H. Lumbroso, *ibid.*, **49**, 394 (1952).

[4] T. B. Johnson and L. H. Levy, *Amer. Chem. J.*, **38**, 456 (1907).

(5%)[4] or with acetone (5%). Lending further support to the structural assignment of **6** was confirmation of its isomerization,[4] in the melt (>140°), to the corresponding isothiocyanate (**7**). Because of its characteristic intense infrared absorption at 2010 cm^{-1}, **7** could be easily detected and the course of the isomerization followed. (It could likewise be confirmed that the isothiocyanate was not present in the product mixture from which **6** was isolated.)

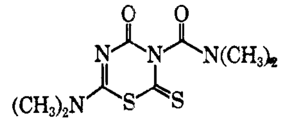
Attempts to isomerize the thiocyanate **6** failed under conditions similar to those employed with ethoxycarbonyl thiocyanate (**1**). Solutions of **6** in acetone, acetonitrile, methyl ethyl ketone, or dimethylformamide, in which potassium thiocyanate had been dissolved, showed no indication of isothiocyanate **7** after several days of heating.

Attention was next turned to the dialkylcarbamoyl thiocyanates. The reaction of dimethylcarbamoyl[5] chloride (**8**) with potassium thiocyanate in acetonitrile gave a liquid which was confirmed as dimethylcarbamoyl isothiocyanate (**9**) on the basis of elemental analysis and the similarity of its infrared spectral properties to those of other acyl isothiocyanates.[1,6]

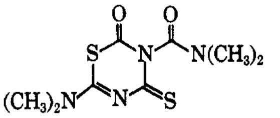


$$\underset{\mathbf{8}}{(CH_3)_2N\overset{O}{\overset{\|}{C}}Cl} \xrightarrow[\text{(or }Pb(SCN)_2/C_6H_6)]{KSCN/CH_3CN} \underset{\mathbf{9}}{(CH_3)_2N\overset{O}{\overset{\|}{C}}NCS}$$

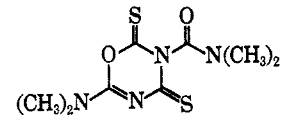
No indication of the presence of the thiocyanate, **17**, in the reaction mixture was found. Similarly, lead thiocyanate in benzene effected conversion only into isothiocyanate **9**. In both reactions leading to the formation of **9**, small amounts of two solid compounds were found. The minor product was isolable, in our hands, only by crystallization from the crude product mixture. This was shown to be the rearranged dimeric compound **10**.[6] The major crystalline product was obtainable from the crude product mixture, or by allowing the purified monomer **9** to stand at room temperature for several weeks. It was assigned the isomeric structure **11** on the basis of infrared absorption at 1720, 1680 (C=O), and 1580 cm^{-1} (C=N); nmr (deuteriochloroform) singlets of equal area at τ 7.06, 6.85, 6.82, and 6.67; and a molecular weight determination. It is likely that **11** is derived from the initially formed "normal" dimer[7] through a carbon–oxygen bond ring opening, rotation, and ring-closure sequence. No trace of **11a**, however, could be detected during the formation of **11** either by heating monomeric **9** for several days or allowing it to stand at ambient temperature for several months. Lending additional support to this structure was our observation of the rapid dimerization of neat dimethylthiocarbamoyl isothiocyanate (**12**) to dimer **13**. The spectral properties of this dimer and those of **11** are quite similar.



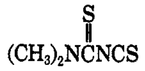
10



11

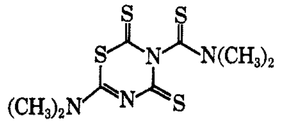


11a



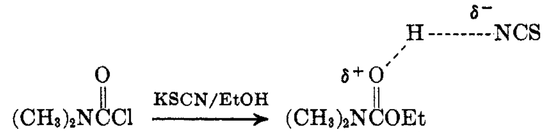
$(CH_3)_2N\overset{S}{\overset{\|}{C}}NCS$

12



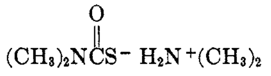
13

To further investigate the effects of solvent, ethanol was employed as the solvent for the reaction between dimethylcarbamoyl chloride and potassium thiocyanate. The product, ethyl dimethylcarbamate hydrothiocyanate (**14**) and its unique properties have been previously described.[8]



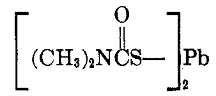
14

In a successful attempt at the synthesis of dimethylcarbamoyl thiocyanate (**17**), dimethylamine was treated with carbonyl sulfide giving the dimethylammonium salt of dimethylthiocarbamic acid (**15**). This was treated with lead acetate giving the corresponding lead salt (**16**). When **16** was treated with cyanogen bromide, a mixture of two compounds resulted. Infrared absorption at 2160 cm^{-1} (–SCN) indicated that one of these was the desired thiocyanate, **17**. The other component was assumed to be dimethylcarbamoyl disulfide (**18**). All attempts to isolate pure **17** failed, as it was found to undergo slow isomerization to isothiocyanate even at room temperature. Distillation of the crude reaction mixture gave only the isomerized product, **9**. The crude mixture containing the thiocyanate was heated in acetone solution and the course of the isomerization was followed by the changes in thiocyanate and isothiocyanate infrared absorptions. The isomerization appeared to be complete within 45 min at reflux temperature. Most important, the additional presence of dissolved potassium thiocyanate had no observable effect on the rate of isomerization.



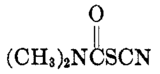
$(CH_3)_2N\overset{O}{\overset{\|}{C}}S^- \; H_2N^+(CH_3)_2$

15



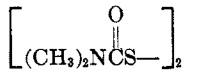
$\left[(CH_3)_2N\overset{O}{\overset{\|}{C}}S—\right]_2Pb$

16



$(CH_3)_2N\overset{O}{\overset{\|}{C}}SCN$

17



$\left[(CH_3)_2N\overset{O}{\overset{\|}{C}}S—\right]_2$

18

The rapid isomerization of dimethylcarbamoyl thiocyanate (**17**) is quite surprising when compared with its diphenyl analog **6**, and ethoxycarbonyl thiocyanate (**1**). If the addition–elimination mode of isomerization were strictly followed, the reactivity sequence **1** > **6** > **17** might be anticipated on the basis of the relative electron-donating capabilities of the carbonyl substituents. The actually observed sequence, **17** > **1** > **6**, coupled

---

[5] Dimethylcarbamoyl chloride in this and subsequently described reactions gave results identical with those of its homolog, dimethylcarbamoyl chloride.

[6] A recent report [J. Goerdler and D. Wobig, *Angew. Chem.*, **79**, 272 (1967)] is in agreement with these structural assignments.

[7] The related imidoylisothiocyanates have been shown to dimerize in a similar manner giving a "normal" dimer; see H. M. Blatter and H. Lukaszewski, *Tetrahedron Lett.*, 1087 (1964).

[8] L. A. Spurlock and P. E. Newallis, *J. Org. Chem.*, **30**, 2086 (1965).

with the lack of effect of thiocyanate ion on the isomerizations of **17** and **6**, indicate that the carbamoyl derivatives do not isomerize by an addition–elimination course. It seems likely, rather, that a simple dissociation–recombination (possibly intramolecular) course, analogous to isomerizations of some alkyl thiocyanates,[9] is preferred in this case.

In light of this preliminary evidence, it appears that there is electronic overlap by the carbamoyl nitrogen with the carbonyl π system which retards isomerization of these thiocyanates by the addition–elimination sequence. The facile thiocyanate ion catalyzed isomerization of **1** is, however, more realistically explained by the bimolecular process. A quantitative estimate of the effect of overlap must await kinetic studies of these systems.

Experimental Section[10]

Diphenylcarbamoyl Thiocyanate (6).—A mixture of 25 g (0.11 mol) of diphenylcarbamoyl chloride and 10.6 g (0.11 mol) of potassium thiocyanate was heated to reflux, with stirring, for 24 hr in 220 ml of acetonitrile.[11] The mixture was cooled, the precipitate removed by filtration, and the filtrate evaporated to remove the solvent. The semisolid residue was taken up in hot chloroform, filtered, and ether added to precipitate the product. A total of 8.9 g (35%) of white crystals was collected, mp 136–138° (lit.[4] mp 138°).

Anal. Calcd for $C_{14}H_{10}N_2OS$: C, 63.28; H, 4.28; N, 11.96; S, 13.67. Found: C, 63.01; H, 4.27; N, 12.16; S, 13.74.

Isomerization of 6 to Diphenylcarbamoylisothiocyanate (7).—A small amount of pure **6** was placed on the heated stage of a Fisher-Johns melting point apparatus and the temperature raised to 140°. Samples of the melt were removed periodically and the infrared spectra examined. Noticeable within 5 min was the appearance of broad absorption at 2010 cm^{-1} (-NCS). A gradual increase of this absorption was accompanied by a corresponding decrease of the thiocyanate absorption at 2160 cm^{-1} until, after 2 hr, the presence of **6** could not be detected. The product, **7**, was a yellow oil which could not be induced to crystallize. No further attempts were made at purification.

Attempted Isomerization of 6 with Thiocyanate Ion.—Approximately 0.1 *M* solutions of **6** were prepared in acetone, acetonitrile, methyl ethylketone, and dimethylformamide. To 10-ml aliquots of each was added 0.100 g of potassium thiocyanate; the solution was sealed in a glass tube. The tubes were heated at 120° for 74 hr, cooled, and the contents removed and poured into 50 ml of water. The product was extracted with two 10-ml portions of methylene chloride, the combined solutions were washed twice with water and dried, and the solvent was evaporated. Examination of the residues (recovered in 94–96% yield) revealed no differences in infrared absorption from that of pure **6**. There was no evidence for the presence of **7**.

Dimethylcarbamoyl Isothiocyanate (9). A. Acetonitrile Method.—To 25 g (0.234 mol) of dimethylcarbamoyl chloride, being stirred and heated at reflux in 150 ml of acetonitrile, was added 22.7 g (0.234 mol) of potassium thiocyanate, in small portions over 1 hr. The resulting slurry was stirred and heated for an additional 2 hr, cooled, and the precipitate removed by filtration. The solvent was evaporated and the residue was taken up in ether, washed with water, dried, and the ether evaporated. Distillation of the crude product gave 14.9 g (40%) of pure **9**: bp 50–51° (0.8 mm); $n^{25}D$ 1.5473; infrared spectrum (film), 1990, 1705, 1370, 1255, 1155, and 870 cm^{-1}.

Anal. Calcd for $C_4H_6N_2OS$: C, 36.92; H, 4.62; N, 2153; S, 24.63. Found: C, 37.01; H, 4.61; N, 21.39; S, 24.57.

1,1-Dimethyl-4-thiobiuret was prepared by the reaction of freshly distilled **9** with anhydrous ammonia in ether. Recrystallization from ether–pentane gave white needles, mp 189–190°.

Anal. Calcd for $C_4H_9N_3OS$: C, 32.64; H, 6.19; N, 28.55; S, 21.75. Found: C, 32.77; H, 6.20; N, 28.57; S, 21.60.

B. Benzene Method.—To 25 g (0.234 mol) of dimethylcarbamoyl chloride dissolved in 200 ml of benzene was added 75 g (0.234 mol) of lead thiocyanate. The slurry was heated, stirred at reflux for 24 hr and cooled, the precipitate removed by filtration, and the filtrate concentrated to remove benzene. Distillation of the residue gave 5.1 g (14%) of **9**, bp 50–52° (0.8 mm), identical with that previously obtained using acetonitrile and potassium thiocyanate.

Diethylcarbamoyl Isothiocyanate.—Analogous preparations by method A and method B gave, respectively, 42 and 15% yields of diethylcarbamoyl isothiocyanate: bp 65–67° (0.1 mm); $n^{25}D$ 1.5546; infrared spectrum (film), 1990, 1705, 1420, 1260, 1155, and 840 cm^{-1}.

Anal. Calcd for $C_6H_{10}N_2OS$: C, 45.55; H, 6.37; N, 17.70; S, 20.27. Found: C, 45.67; H, 6.39; N, 17.46; S, 20.17.

1,1-Diethyl-4-thiobiuret was prepared and recrystallized from ether–pentane, giving white needles, mp 89.5–90.0°.

Anal. Calcd for $C_6H_{13}N_3OS$: C, 41.20; H, 7.58; N, 24.00; S, 18.28. Found: C, 41.27; H, 7.66; N, 24.00; S, 18.53.

2-Dimethylamino-5-dimethylcarbamoyl-6-thiono-1,3,5-thiadiazin-4-one (10).—A 20% solution of 16.0 g of freshly prepared crude **9** in benzene was allowed to stir at room temperature for 3 days. At the end of this time 200 g of a solid was collected. Recrystallization from acetonitrile gave greenish white crystals: mp 199.0–199.5° dec (lit.[6] mp 198–199° dec); nmr (20% DMSO-d_6), τ 6.88 (singlet), 6.87 (singlet), 6.83 (singlet), 6.71 (singlet); ultraviolet spectrum (CH_3CN) 268 mμ (ϵ 10,300).

Anal. Calcd for $C_8H_{12}N_4O_2S$: C, 36.92; H, 4.62; N, 21.53; S, 24.63; mol wt, 260. Found: C, 36.89; H, 4.61; N, 21.59; S, 24.72; mol wt, 256.

2-Dimethylamino-5-dimethylcarbamoyl-4-thiono-1,3,5-thiadiazin-6-one (11).—A portion of crude **9** from which **10** had been removed (or distilled material which had been allowed to stand, neat, at room temperature for several weeks) deposited a deep yellow solid residue. Recrystallization of this material from ether–chloroform gave pale yellow crystals: mp 134.5–135.0°; infrared spectrum (mull), 1720, 1680, 1580, 1270, 1185, 760 and 750 cm^{-1}; nmr (20% $CDCl_3$), τ 7.06 (singlet), 6.85 (singlet), 6.82 (singlet), 6.67 (singlet); ultraviolet spectrum (CH_3CN), 240 mμ (ϵ 24,000), 299 mμ (ϵ 12,000).

Anal. Calcd for $C_8H_{12}N_4O_2S_2$: C, 36.92; H, 4.62; N, 21.53; S, 24.63; mol wt, 260. Found: C, 36.87; H, 4.62; N, 21.47; S, 24.41; mol wt, 254.

Dimethylthiocarbamoyl Isothiocyanate (12).—Dimethylthiocarbamoyl chloride[12] was allowed to react with potassium thiocyanate by method A for preparation of carbamoyl isothiocyanates, giving dimethylthiocarbamoyl isothiocyanate (40%). As the product was unstable to distillation, no further purification was attempted.

1,1-Dimethyldithiobiuret was prepared by the immediate reaction of freshly prepared isothiocyanate with anhydrous ammonia in ether. The biuret was recrystallized from ether–pentane as yellow needles, mp 195–196°.

Anal. Calcd for $C_4H_9N_3S_2$: C, 29.42; H, 5.56; N, 25.74; S, 39.28. Found: C, 29.49; H, 5.59; N, 25.50; S, 39.42.

2-Dimethylamino-5-dimethylthiocarbamoyl-1,3,5-thiadiazin-4,6-dithione (13).—Monomeric dimethylthiocarbamoyl isothiocyanate was allowed to stand at room temperature for 2 days. At the end of this time the liquid had completely solidified. Recrystallization of the solid from methylene chloride–ether gave a near quantitative yield of orange crystals: mp 159.5–160.0°; infrared spectrum (mull), 1580, 1520, 1265, 1180, 1140, 960, and 795 cm^{-1}; nmr (20% $CDCl_3$), τ 6.85 (singlet), 6.78 (singlet), 6.65 (singlet), 6.58 (singlet); ultraviolet spectrum (CH_3CN), 285 mμ (ϵ 24,000), 360 mμ (ϵ 12,800).

Anal. Calcd for $C_8H_{12}N_4S_4$: C, 32.85; H, 4.14; N, 19.16; S, 43.85; mol wt, 292. Found: C, 32.76; H, 4.14; N, 19.05; S, 44.05; mol wt, 290.

---

[9] For recent examples, see A. Fava, A. Iliceto, A. Ceccon, and P. Koch, *J. Amer. Chem. Soc.*, 87, 1045 (1965); L. A. Spurlock and P. E. Newallis, *Tetrahedron Lett.*, 303 (1966).

[10] Melting points are corrected and boiling points are uncorrected. Ir spectra were determined with a Perkin-Elmer Infracord using sodium chloride optics. The nmr determination was carried out on a Varian Associates A-60 spectrometer; approximately 20% solutions in $CDCl_3$ were employed with tetramethylsilane as the internal standard. Analyses and molecular weight determinations were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

[11] A similar quantity of absolute ethanol or acetone may be employed as the solvent. Yields of product are, however, markedly reduced.

[12] R. H. Goshorn, W. W. Levis, E. Jaul, and E. J. Riher, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 307.

Dimethylammonium N,N-Dimethylthiocarbamate (15).—Into a solution of 18 g (0.4 mol) of dimethylamine in 200 ml of absolute ether at 0° was bubbled carbonyl sulfide at such rate that the temperature did not rise above 5°. The gas was added until the reaction was no longer exothermic and then the slurry was stirred at 0° for 1 hr. The product, 27.8 g (46%), was collected by filtration and washed with ether. No further purification was attempted.

Lead N,N-Dimethylthiocarbamate (16).—To a stirred solution of 11.7 g (0.08 mol) of dimethylammonium salt, **15**, in 50 ml of water was added a solution of 25.5 g (0.08 mol) of lead acetate in 100 ml of water. Precipitation was immediate; however, the mixture was stirred for an additional 1 hr to ensure completeness of reaction. The product was collected by filtration and washed twice with acetone and finally twice with ether. The crystals were dried for 48 hr under vacuum affording 10.0 g (31%) of lead salt.

Dimethylcarbamoyl Thiocyanate (17) and Dimethylcarbamoyl Disulfide (18).—A slurry of 10.0 g (0.025 mol) of lead salt **16** and 6.0 g (0.056 mol) of dry cyanogen bromide in 50 ml of anhydrous benzene was stirred for 5 days at room temperature. The precipitate was removed by filtration and the filtrate was washed twice with 100-ml portions of water. The solution was dried and the solvent evaporated under vacuum keeping the temperature below 25°, giving 7.9 g of a mixture of **17** and **18**. The product mixture was an orange oil which resisted all attempts at separation of its components: infrared spectrum (film), 2160, 1710, 1675, 1360, 1245, 1090, and 680 cm^{-1}. It was stored at −20° for further use since a sample was discovered to isomerize substantially on standing, neat, for 2 days at room temperature.

Isomerizations of 17 to Dimethylcarbamoyl Isothiocyanate (9).—Distillation of 5.0 g of the crude mixture of **17** and **18** gave 1.2 g of the isomerized product, **9**, bp 40–42° (0.1 mm). No indication of the thiocyanate **17** could be discovered in the distillate or tarry pot residue.

A solution of 1.0 g of the thiocyanate–disulfide mixture in 10 ml of acetone was heated at reflux and the course of the isomerization followed by infrared. The characteristic -NCS absorption of **9** at 1990 cm^{-1} was observable after 5 min. The isomerization was assumed to be complete after 45 min with the complete disappearance of the -SCN absorption at 2160 cm^{-1}. When 0.5 g of potassium thiocyanate was additionally dissolved in the acetone solution the time for complete isomerization was again approximately 45 min. The dissolved salt gave no observable accelerating effect to the isomerization.

Registry No.—**6**, 4917-81-1; **7**, 3553-71-7; **9**, 16011-79-3; **10**, 14004-91-2; **11**, 16011-81-7; **13**, 16011-82-8; **17**, 16011-83-9; **18**, 16011-88-4; 1,1-dimethyl-4-thiobiuret, 16011-84-0; diethylcarbamoyl isothiocyanate, 16011-85-1; 1,1-diethyl-4-thiobiuret, 16011-86-2; 1,1-dimethyldithiobiuret, 14812-36-3.

Reaction of Chloral with Hydrazine

C. N. Yiannios, A. C. Hazy, and J. V. Karabinos

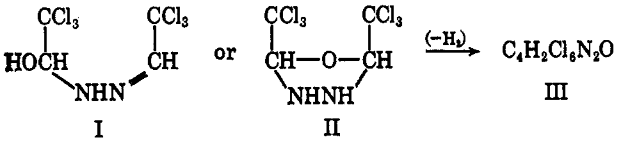
Olin Research Center, New Haven, Connecticut 06504

Received October 3, 1967

The reaction of chloral with hydrazine has been reinvestigated. Two products, trichloroethylidene trichloroacetic acid hydrazide and dichloroethylidene trichloroacetic acid hydrazide, were isolated and their structures were elucidated by spectral methods.

G. Knöpfer[1] reported the isolation of an "anhydrochloral" hydrazine derivative prepared by heating either hydrazine sulfate or hydrochloride in an excess of chloral hydrate.

Elemental analysis led to the assignment of the empirical formula $C_4H_2Cl_6N_2O$ to this product (III). When the compound was decomposed with aqueous potassium hydroxide, Knöpfer failed to isolate any chloroform. He proposed that this derivative resulted from dehydrogenation of either structure I or II, but favored II as the precursor since its isomer (I) should have been decomposed by alkali to give chloroform.



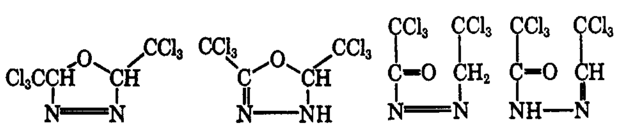
I II III

Compound III was subsequently prepared by Knöpfer[2] from hydrazine hydrate and chloral hydrate in glacial acetic acid. Upon investigation of the analogous reaction of hydrazine hydrate and bromal hydrate, Knöpfer discovered that, in the absence of a solvent, a product having the empirical formula $C_4H_2Br_6N_2O$ was produced. This same reaction in glacial acetic acid, however, gave a pentabromo derivative of formula $C_4H_3Br_5N_2O$. No mention was made of any analogous pentachloro derivative.

The present investigation sheds considerable light on the reaction of chloral with hydrazine. In addition to elucidating the structure of compound III, several other products, including a pentachloro derivative, have been obtained and identified.

Results and Discussion

Compound III was prepared from excess chloral hydrate and monohydrazine sulfate or chloral hydrazine $[Cl_3CCH(OH)NHNH_2]$. Knöpfer's[2] method (in glacial acetic acid) also gave III. The infrared spectra of samples obtained by either method were identical; the elemental analyses compared favorably with those reported by Knöpfer.[1] Several likely structures fitting the formula $C_4H_2Cl_6N_2O$ (IIIa–d) may be considered.



IIIa IIIb IIIc IIId

Evidence accumulated during this investigation points overwhelmingly to the acyclic structure IIId. The infrared spectrum (KBr pellet) showed absorption at 3.1 (m, secondary amide N—H stretch), 3.3 (w, H—C= vibration) and 5.83 μ (s, C=O stretch). Although the carbonyl absorption appeared at a lower wavelength than would be expected for an aliphatic secondary amide, this position coincides with that

---

[1] G. Knöpfer, *Monatsh. Chem.*, **34**, 769 (1913).

[2] G. Knöpfer, *ibid.*, **37**, 357 (1916).