

## Derivatives of Hydrazine. X. The Reaction between Thiophosgene and Semicarbazide or Thiosemicarbazide

UFFE ANTHONI and PER HALFDAN NIELSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark

The reaction between thiophosgene and semicarbazide previously reported to give an *N*-isothiocyanatoamine has been shown by combined physical and chemical evidence to give instead bis(2-amino-1,3,4-oxadiazol-5-yl) trithiocarbonate. In the same way, the corresponding reaction between thiophosgene and thiosemicarbazide has been shown to give bis(2-amino-1,3,4-thiadiazol-5-yl) trithiocarbonate. A logical scheme to encompass the formation and reactions of these compounds is suggested.

The reaction between thiophosgene and hydrazine derivatives generally affords thiocarbonylhydrazides. However, if carried out in aqueous hydrochloric acid other compounds, claimed by Beckett and Dyson<sup>1</sup> to be *N*-isothiocyanatoamines, are sometimes the main products. In the aromatic series it has previously been shown<sup>2</sup> that the product formed by the action of thiophosgene on 1,1-diphenylhydrazine is, in fact, 2-thiocyanatodiphenylamine formed by rearrangement of the very unstable *N*-isothiocyanatodiphenylamine. The reaction between thiophosgene and 1-methyl-1-phenylhydrazine proceeds in a similar way.<sup>3</sup> Aliphatic *N*-isothiocyanatoamines are also very unstable,<sup>4</sup> undergoing dimerisation<sup>5</sup> except when sterically hindered.<sup>6</sup> These results indicate that the products obtained by Beckett and Dyson, reported to be stable at room temperature, very probably do not contain the N—NCS grouping.

The present paper summarises the results obtained by reinvestigating the products from thiophosgene and semicarbazide (*1a*) or thiosemicarbazide (*1b*) in aqueous hydrochloric acid. They were formulated by Beckett and Dyson as *N,N'*-bis(isothiocyanato)-*N,N'*-biscarbamoyl-

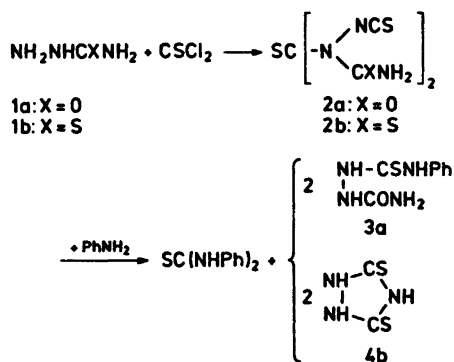


Fig. 1.

thiourea (*2a*) and the corresponding thiocarbonyl derivative (*2b*) as shown in Fig. 1.

The structural proof for *2a* and *2b* was based on the reaction with aniline, which gave 1,3-diphenylthiourea and 1-(phenylthiocarbonyl)semicarbazide (*3a*) or dithiourazole (*4b*), respectively. Since 4,4-diphenylsemicarbazide reacted analogously to *1a*, isomeric forms of *2a* and *2b* were not considered likely.

Using techniques not available at the time of the earlier work, we have reformulated the reaction between *1b* and thiophosgene as shown in Fig. 2. The reaction affords a compound  $\text{C}_6\text{H}_4\text{N}_4\text{S}_3$ , compatible with both structures *2b* and *4b*. The IR spectrum in KBr discs, however, is devoid of absorption in the region between  $1700 \text{ cm}^{-1}$  and  $2700 \text{ cm}^{-1}$ , excluding the presence of both the —NCS and the —SCN grouping.<sup>3,4</sup> Accordingly, formula *2b* cannot be correct for this compound. The reaction with aniline gave, in addition to 1,3-diphenylthiourea, a

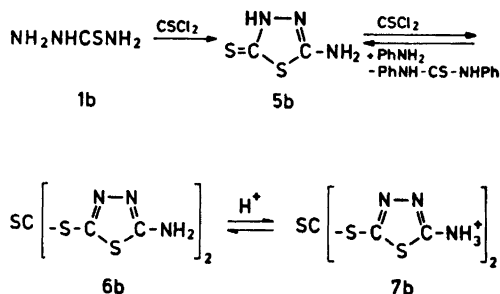


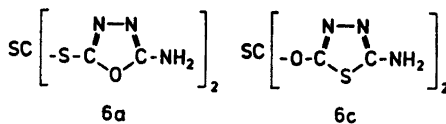
Fig. 2.

compound  $\text{C}_8\text{H}_8\text{N}_4\text{S}_3$ . This was formulated by Beckett and Dyson as dithiourazole (4b), but is now known to be, in fact, the isomeric 2-amino-1,3,4-thiadiazoline-5-thione (5b),<sup>7,8</sup> which can be prepared from thiosemicarbazide and carbon disulfide. Since identical products were obtained from the reaction between thiophosgene and 1b or 5b, these can be formulated as 6b. The possibility that thiophosgene instead reacts with the amino group of 5b giving a thiourea seems to be excluded by the observation that 1b and thiophosgene in acetone give the dihydrochloride of 6b, 7b, with an IR spectrum showing only the expected changes from protonation of the amino groups. Furthermore, 6b is a trithiocarbonate which is expected to react with aniline to give 5b and 1,3-diphenylthiourea<sup>9</sup> whilst a thiourea is not expected to show this reaction.

The formation of 6b from 1b very probably proceeds *via* formation of 5b as indicated in Fig. 2. The formation of 2b or any other *N*-isothiocyanatoamine as an intermediate is considered very unlikely. First, if 2b acts as an intermediate, a rearrangement to 6b would involve simultaneous rearrangement of the thiocarbonyl group to the sulfur atoms of both NCS groups. Second, it is well known that the attack of *N*-NCS on thioamides affords nitriles,<sup>10</sup> and therefore a mechanism proceeding *via*, *e.g.*,  $\text{NH}_2\text{CSNHCS}$  is not expected.

Next the constitution of the reaction product from 1a and thiophosgene was considered. A comparison of the physical and chemical properties with those of 6b pointed to a similar structure. Thus, the IR spectra in KBr were almost identical in the range from 1000–4000  $\text{cm}^{-1}$ , expect that the two strong bands at 1135 and 1500  $\text{cm}^{-1}$  in 6b were displaced to two doublets at 1170+1180  $\text{cm}^{-1}$  and 1595+1608

$\text{cm}^{-1}$ . Mass spectrometry established that pyrolysis of 6b afforded substantial amounts of  $\text{CS}_2$ , while the product in question gave mixtures of  $\text{CS}_2$  and COS with a percentage of COS ranging from 10 to 100, depending on the temperature and duration of the pyrolysis. Since elemental analysis established the formula  $\text{C}_8\text{H}_8\text{N}_4\text{O}_8$ , either structure 6a or 6c was possible.



The changes in the IR spectrum undoubtedly arise from the shift of two skeletal stretching frequencies, but both formulas are consistent with this result. However, the reaction with aniline gave 1,3-diphenylthiourea and 1-(phenylthiocarbamoyl)semicarbazide in confirmation of the results stated by Beckett and Dyson, while 1-(phenylcarbamoyl)thiosemicarbazide was not formed. This was definitely proved by comparison with authentic samples of both compounds, prepared from  $\text{PhNCS}$  and semicarbazide and from  $\text{PhNCO}$  and thiosemicarbazide, respectively. This leaves no doubt that the correct structure of the reaction product from thiophosgene and 1a is 6a. (Of course, a "mixed" product, containing both the oxadiazolyl moiety of 6a and the thiadiazolyl moiety of 6c, is excluded by the same observation).

Further discussion of the structure of 6a and 6b, based on  $^{13}\text{C}$  NMR spectroscopic investigations, will be presented in a forthcoming paper.

## EXPERIMENTAL

Analyses were carried out at the Microanalysis Department of this laboratory. The melting points were determined in capillary tubes on a Büchi melting point apparatus and are not corrected. The infrared spectra were recorded on a Perkin Elmer Model 337 Grating Infrared Spectrophotometer. Mass spectra of the pyrolysis products from 6b were obtained on a Finnigan 1015 S/L combined gas chromatograph-mass spectrometer.

*1-(Phenylthiocarbamoyl)semicarbazide (3a)*. This compound was prepared following the directions given by Arndt *et al.*<sup>11</sup> The yield was 75%, m.p. 201–202°C. (Found: C 45.95; H 4.83; N 26.75; S 15.43. Calc. for  $\text{C}_8\text{H}_{10}\text{N}_4\text{OS}$ : C 45.71; H 4.80; N 26.66; S 15.86).

*2-Amino-1,3,4-thiadiazoline-5-thione (5b)*. An authentic sample of this compound was prepared by Sandström's method.<sup>9</sup> The yield was 65 %, m.p. 234–235 °C. (Found: C 18.06; H 2.47; N 30.98. Calc. for  $C_2H_2N_3S_2$ : C 18.05; H 2.47; N 31.58).

*Bis(2-amino-1,3,4-thiadiazol-5-yl) trithiocarbonate (6b)*. *Method A*. 2-Amino-1,3,4-thiadiazoline-5-thione (0.1 mol) was suspended in water (50 ml) and shaken with thiophosgene (0.05 mol) for 2 h. The precipitate was collected and dried. The compound was dissolved in dimethyl sulfoxide and reprecipitated with water. The yield was almost quantitative. M.p. 240–250 °C. (Found: C 19.80; H 1.37; N 26.91; S 52.10. Calc. for  $C_4H_4N_6S_3$ : C 19.47; H 1.31; N 27.28; S 51.95).

*Method B*. The directions given by Beckett and Dyson<sup>1</sup> were followed. The compound decomposed on attempted recrystallisation and was therefore purified by dissolution in dimethyl sulfoxide and reprecipitation with cold acetone. The analyses given below refer to the crude product. M.p. 240–250 °C decomp. The yield was 60 %. (Found: C 20.21; H 1.60; N 26.39; S 51.06). This compound was proved to be identical with the sample prepared as described under A by their IR and mass spectra and by mixture melting points.

*Bis(2-amino-1,3,4-thiadiazol-5-yl) trithiocarbonate dihydrochloride (7b)*. 2-Amino-1,3,4-thiadiazoline-5-thione (0.1 mol) was dissolved in acetone (50 ml) and thiophosgene (0.05 mol) was added in one portion. The crystalline yellow precipitate was filtered off and dried. (Found: C 15.91; H 1.52; N 21.88. Calc. for  $C_6H_8N_6S_3Cl_2$ : C 15.73; H 1.59; N 22.04). On treatment with aqueous base, *6b* was liberated.

*Bis(2-amino-1,3,4-oxadiazol-5-yl) trithiocarbonate (6a)*. The directions given by Beckett and Dyson<sup>1</sup> were followed. The compound could not be recrystallized, but it was reprecipitated from dimethyl sulfoxide and water. M.p. 185–194 °C decomp. The yield was 25 %. (Found: C 21.56; H 1.53; N 29.95; S 34.23. Calc. for  $C_6H_4O_2S_3$ : C 21.73; H 1.46; N 30.42; S 34.81).

*1-(Phenylcarbamoyl)thiosemicarbazide*. This compound was prepared following the directions given by Freund and Schander.<sup>12</sup> The yield was 70 %, m.p. 216–217 °C. (Found: C 45.66; H 4.85; N 26.81. Calc. for  $C_8H_{10}N_4OS$ : C 45.71; H 4.80; N 26.66).

5. Anthoni, U., Larsen, C. and Nielsen, P. H. *Acta Chem. Scand.* 22 (1968) 309.
6. Anthoni, U., Larsen, C. and Nielsen, P. H. *Acta Chem. Scand.* 21 (1967) 2061.
7. a. Petrow, V., Stephenson, O., Thomas, A. J. and Wild, A. M. *J. Chem. Soc.* (1958) 1508; b. Guha, P. C. *J. Amer. Chem. Soc.* 44 (1922) 1502, 1510.
8. Sandström, J. *Acta Chem. Scand.* 15 (1961) 1295, p. 1300.
9. Delépine, M. and Schwing, P. *Bull. Soc. Chim. Fr.* (4) 7 (1909) 895.
10. Anthoni, U., Larsen, C. and Nielsen, P. H. *Acta Chem. Scand.* 21 (1967) 2580.
11. Arndt, F., Milde, E. and Tschenscher, F. *Ber. Deut. Chem. Ges.* 55 (1922) 341, p. 349.
12. Freund, M. and Schander, A. *Ber. Deut. Chem. Ges.* 29 (1896) 2500, p. 2510.

Received January 7, 1974.

## REFERENCES

1. Beckett, T. and Dyson, G. M. *J. Chem. Soc.* (1937) 1358.
2. Anthoni, U., Larsen, C. and Nielsen, P. H. *Acta Chem. Scand.* 21 (1967) 1201.
3. Anthoni, U., Larsen, C. and Nielsen, P. H. *To be published*.
4. Anthoni, U., Larsen, C. and Nielsen, P. H. *Acta Chem. Scand.* 20 (1966) 1714.