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N-Isothiocyanatoamines

II. The Synthesis and Rearrangement of *N*-Isothiocyanatodiphenylamine

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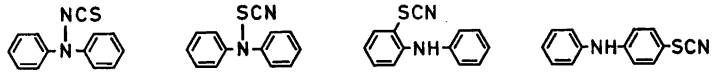
The reaction between *N*,*N*-diphenyldithiocarbazic acid and dicyclohexylcarbodiimide at −80°C has been studied. It is shown that the *N*-isothiocyanatodiphenylamine initially formed rapidly rearranges to 2-thiocyanatodiphenylamine if the temperature is allowed to rise. The latter compound is also obtained from the reaction of *N*,*N*-diphenylhydrazine with thiophosgene. The formation of *N*-isothiocyanatodiphenylamine as an intermediate in this reaction is indicated by infrared spectroscopy and by formation of 1,1,4-triphenylthiosemicarbazide on addition of aniline.

In Part I of this series,[1] we described the preparation of *N*-isothiocyanatodiethylamine and demonstrated that rapid dimerization occurred at room temperature. Also, a compound prepared by Podgornaya *et al.*[2] and regarded as *N*-isothiocyanatopiperidine was shown to be, in fact, *N*,*N*-pentamethylenehydrazinium *N*,*N*-pentamethylenedithiocarbazate.

To study the influence of structure on the stability of *N*-isothiocyanatoamines, we have now examined the reaction between thiophosgene and *N*,*N*-diphenylhydrazine, reported by Beckett and Dyson[3] to yield *N*-isothiocyanatodiphenylamine (I). However, their product (hereafter referred to as *A*) could not be induced to react with alcohol, and with aniline no isolable product was obtained though *N*-isothiocyanatodiphenylamine would be expected to form 1,1,4-triphenylthiosemicarbazide. It is difficult to reconcile these properties with the postulated formula, and it appeared to us that the product could be a thiocyanatodiphenylamine such as (II), (III), or (IV).



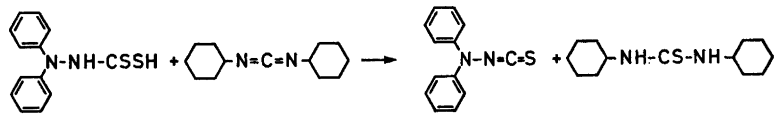
I II III IV

The analytical data are consistent with all four formulae. However, *A* exhibited no infrared bands indicative of the N=C=S grouping, but showed a medium-strength, narrow absorption band at 2165 cm^{-1} (in CCl_4) characteristic for aromatic thiocyanates.[4] In addition, absorption in the N—H stretching vibration region (a triplet centered at 3345 cm^{-1} in KBr, 3420 cm^{-1} in CCl_4) definitely excludes the structures (I) and (II). Evidence in support of structure (III) or (IV) was deduced from the mass spectrum of *A*. Phenyl isothiocyanate is known [5] to produce $C_6H_5^+$ as a prominent fragment on electron impact. Jensen *et al.*[6] have discussed the difference between the mass spectra of aliphatic thiocyanates and isothiocyanates. In both types of compounds peaks were observed corresponding to fragments formed by elimination of $HSCN^+$ (or $HNCS^+$). However, butyl and hexyl thiocyanate showed additional peaks attributed to M—HCN, which, as expected, were absent in the spectra of the corresponding isothiocyanates. The mass spectrum of *A* shows, in addition to the molecular ion (*m/e* 226), peaks corresponding to M—HCN (*m/e* 199), and M—HSCN (*m/e* 167). A further series of prominent peaks at *m/e* 225, 198, and 166 probably arises from a fragmentation of the M—1 ion analogous to that of the molecular ion. Attention was therefore turned to the synthesis of the compounds (III) and (IV).

The *p*-isomer, (IV), was obtained in good yield from the reaction of diphenylamine with $(SCN)_2$, but proved to be different from *A*. However, the presence of a sharp peak at 2157 cm^{-1} in the IR-spectrum of (IV) fully substantiated the presence of a thiocyanate group in *A*. Attempts to prepare 2-thiocyanatodiphenylamine from 2-mercaptodiphenylamine [7] and cyanogen bromide were unsuccessful as were attempts to hydrolyze *A* to the thiol. The infrared spectra of these two compounds (in CCl_4), however, were almost superimposable apart from the absorptions due to the SH- (2540 cm^{-1}) and SCN- (2160 cm^{-1}) groups. Since the nature of the *S*-substituent can have only little influence on the infrared spectrum of the diphenylamine moiety, compound *A* is concluded to have the structure III.

In our initial attempts to synthesize *N*-isothiocyanatodiphenylamine (I), the stable and easily accessible 1-(*N*,*N*-diphenylthiocarbazoyl)-1,2,4-triazole was used as starting material. A series of thermolysis experiments were carried out under varying conditions of heating, pressure *etc.*, but no products other than 2-thiocyanatodiphenylamine (III) were observed. To eliminate the possibility of an intramolecular rearrangement, a low-temperature method was clearly needed.

The ready availability in this laboratory of dithiocarbazic acids [8] led us to investigate the reaction of diphenyldithiocarbazic acid with dicyclohexylcarbodiimide, which might proceed as follows:



When the reactants dissolved in ether or CCl_4 were allowed to stand for some days at −80°C, a strong infrared band at 1956 cm^{-1} appeared which

did not arise from either of the two reactants alone. The appearance of this band is good evidence for the N=C=S group; *cf.* that absorption at 2010–2040 cm^{-1} has been observed previously for *N*-isothiocyanatodiethylamine.[1] The difference in frequency by about 60 cm^{-1} is close to that reported for alkyl and aryl isothiocyanates.[9] However, all attempts to isolate *N*-isothiocyanatodiphenylamine (I) proved unsuccessful due to its instantaneous rearrangement to (III) at higher temperature as shown by infrared spectroscopy. On the other hand, when aniline was added to the crude solution of (I) in ether, a colourless crystalline product, identified as 1,1,4-triphenylthiosemicarbazide, was obtained in 60 % yield. This is conclusive evidence for the presence of (I) in the cold solution. Studies on the rearrangement of other *N*-isothiocyanatoanilines into (thiocyanatoaryl)amines are in progress.

EXPERIMENTAL

Analyses were carried out at the Microanalysis Department of this laboratory. The infrared spectra (400–4000 cm^{-1}) were recorded using a Perkin-Elmer model 337 grating infrared spectrophometer. The region between 2000 and 2200 cm^{-1} was studied using a scale expander. Nuclear magnetic resonance spectra were obtained on a Varian A-60 instrument with tetramethylsilane as an internal reference. The mass spectra were recorded on an Atlas CH4 mass spectrometer at an ionizing potential of 70 eV.

2-Thiocyanatodiphenylamine (III). This compound was prepared according to the directions given by Beckett and Dyson [3] for the preparation of the supposed *N*-isothiocyanatodiphenylamine. The yield of crude product was 90 %. Extraction with pentane gave a 45 % yield of yellowish crystals, which could be recrystallized from pentane to give colourless needles, m.p. 63–64°C. (Found: C 68.95; H 4.31; N 12.29; S 14.16. Calc. for $C_{13}H_{10}N_2S$: C 68.99; H 4.45; N 12.38; S 14.17). *IR-spectrum* (CCl_4, in cm^{-1}): 3410m, 3062w, 3049w, 2162m, 1602m, 1590s, 1512s, 1503m, 1468m, 1454m, 1416w, 1316s, 1288m, 1218w, 1164w, 1078w, 1028w, 883w, 728m, 696m, 640w, 578w. *Mass spectrum* (most abundant ions, *m/e*; in parenthesis, % relative abundance with the base peak taken as 100 %): 227(12), 226(48), 225(100), 224(6), 200(4), 199(14), 198(22), 168(4), 167(18), 166(8), 154(6), 140(4), 139(4), 122(6), 113(8), 112(6), 96(12), 95(6), 78(8), 77(21), 70(8), 69(11), 65(6), 63(9), 51(25), 50(8), 45(10), 39(9), 28(6), 27(8).

When treated with boiling hydrochloric acid or sodium hydroxide [10] no thiol formation could be detected. Moreover, treatment with cold concentrated sulfuric acid [11] for several days left the compound unchanged (*cf.* that a thiocyanato group in *ortho* position often shows increased stability [11]).

2-Mercaptodiphenylamine was prepared by the method of Gilman *et al.*[7] and was freshly distilled before recording of the spectra. *IR-spectrum* (CCl_4, in cm^{-1}): 3385m, 3063m, 3047w, 2535vw, 1602m, 1590s, 1511s, 1501s, 1466m, 1452m, 1413w, 1313s, 1285w, 1218w, 1161w, 1078w, 1039w, 1028w, 883w, 727m, 693m, 639w, 578w. *Mass spectrum:* 201(100), 200(38), 199(25), 186(22), 169(40), 168(44), 167(33), 154(5), 140(6), 139(6), 96(5), 84(20), 77(32), 70(4), 69(7), 65(9), 63(6), 51(15), 45(8), 39(10), 28(9), 27(13).

Attempts to convert this compound (as well as its sodium or lead(II) salt) into 2-thiocyanatodiphenylamine with BrCN were unsuccessful. On column chromatography of the products more than 50 % of the thiol could be recovered.

4-Thiocyanatodiphenylamine (IV). Bromine (1.6 g) was added portionwise under vigorous shaking and cooling to a suspension of $Pb(SCN)_2$ [12] (3.7 g) in 20 ml of ether. The reaction mixture was filtered and diphenylamine (1.6 g) added to the resulting colourless solution. After standing for 10 min at room temperature, evaporation afforded a red oil which was recrystallized from pentane to give colourless crystals, m.p. 65°C. Infrared data and mixed m.p. with the compound prepared according to Beckett and Dyson [3] from diphenylhydrazine and thiophosgene, showed that the two compounds were not identical. (Found: C 68.90; H 4.47; N 12.54; S 14.29. Calc. for $C_{13}H_{10}N_2S$: C 68.99; H 4.45; N 12.38; S 14.17). *IR-spectrum* (KBr, in cm^{-1}): 3353s, 3340s, 3059w, 2157s, 1606s, 1588vs, 1530vs, 1499s, 1448m, 1403w, 1345s, 1326s, 1294w, 1249w, 1188m, 1175m,

1155w, 1085w, 1029w, 898w, 880w, 834m, 825s, 810m, 750s, 712m, 698m, 675w, 574m, 525m, 504w, 476w.

The structure of the compound (IV) was demonstrated by repeating the preparation given above, using only half the amount of diphenylamine. M.p. and analysis fully confirm Söderbäck's results [13] that a dithiocyanatodiphenylamine was formed. Although previous workers in this field [13,14] have assumed that the product was the 4,4′-isomer (and, accordingly, the monosubstituted intermediate the 4-isomer), a definitive proof was, in fact, required. This was provided by IR and NMR spectroscopy. The infrared spectrum showed no absorptions in the 700—800 cm^{-1} range, but a very strong band at 812 cm^{-1}. These characteristics, coupled with a study of the pattern in the 1600—2000 cm^{-1} region, support the formulation of the compound as the 4,4′-isomer.[15] Again, the pattern arising from the aromatic protons in the NMR-spectrum was consistent with the presence of two A_2B_2 systems.

1-(N,N-Diphenylthiocarbazoyl)-1,2,4-triazole. The procedure for synthesis was essentially that outlined by Staab and Walther [16] for analogous compounds. 1,2,4-Triazole (2.7 g) and thiophosgene (1.1 g) were shaken for 1 h with a mixture of dry ether (150 ml) and carbon tetrachloride (50 ml). The solution was filtered to remove triazolium chloride and added to another solution, prepared by shaking *N,N*-diphenylhydrazinium chloride (2.2 g) and triethylamine (1.1 g) in dry ether for 1 h with subsequent filtration of triethylammonium chloride. The combined solutions were boiled for a short time and allowed to stand for 2 h at room temperature. The solvent was evaporated under reduced pressure and the crude product (1.7 g) recrystallized first from ethanol and then from pentane to give yellowish crystals, m.p. 121—122°C. (Found: C 60.85; H 4.67; N 23.98; S 11.14. Calc. for $C_{15}H_{13}N_5S$: C 60.99; H 4.44; N 23.72; S 10.85).

Thermolysis of 1-(N,N-diphenylthiocarbazoyl)-1,2,4-triazole. Using the apparatus and conditions described earlier,[1] thermal decomposition of the title compound resulted in the formation of 1,2,4-triazole (collected from the glass tube and the receiver) and 2-thiocyanatodiphenylamine (residue in the reaction chamber). Both compounds were identified by comparing with the m.p. and infrared spectra of authentic compounds. Obviously, the volatility of the *N*-isothiocyanatodiphenylamine initially formed in the reaction is insufficient for distillation prior to rearrangement.

Reaction between 1-(N,N-diphenylthiocarbazoyl)-1,2,4-triazole and aniline. The triazole was added to excess aniline in ethanol, and the mixture was heated on a steam bath for 5 min. The solution was then left at room temperature for several days. The colourless crystals (80 % yield) were filtered off and washed with ethanol. The compound so obtained (m.p. 180—181°C) was identical (m.p., mixed m.p., and infrared spectrum) with 1,1,4-triphenylthiosemicarbazide, obtained by the reaction between *N,N*-diphenylhydrazine and phenyl isothiocyanate.[17]

N,N-*Diphenyldithiocarbazic acid.* This was prepared by the method of Stahel.[18] The colourless crystals were only slightly soluble in ether and were found to be quite stable under anhydrous conditions at room temperature for several weeks. The infrared spectrum was anomalous in showing an absorption band at 2420 cm^{-1}, which is that of an SH vibration. The monophenyldithiocarbazic acid, for example, devoid of absorption in the same range, was partly on this basis assigned a dipolar structure.[8] Apparently, the low base strength of the nitrogen atoms in the diphenyldithiocarbazic acid favours the thiol form.

N-*Isothiocyanatodiphenylamine (I).* A solution of *N,N*-diphenyldithiocarbazic acid (0.6 g) in anhydrous ether (75 ml) was added to a solution of dicyclohexylcarbodiimide (0.5 g) in ether (15 ml). After 3 days at −80°C the separated dicyclohexylthiourea was filtered off (40 % yield). Its infrared spectrum and m.p. was identical with that of an authentic specimen. The remaining solution, from which no more dicyclohexylthiourea could be obtained on prolonged standing, showed a strong infrared absorption at 1956 cm^{-1}, which rapidly disappeared on heating to room temperature. At the same time the characteristic peak at 2162 cm^{-1} appeared, showing that rearrangement to 2-thiocyanatodiphenylamine had occurred. The usual work-up gave a 40 % yield of (III), indistinguishable from the compound prepared according to Beckett and Dyson [3] by m.p. and infrared spectrum.

1,1,4-Triphenylthiosemicarbazide. A solution of N-isothiocyanatodiphenylamine in ether prepared as above was treated with a slight excess of aniline. The solution was left for four days at −80°C. The mixture was then filtered and the crystals (61 % yield)

recrystallized once from aqueous ethanol. Mixed melting point with an authentic sample of 1,1,4-triphenylthiosemicarbazide [17] gave no depression, and the infrared spectra were superimposable.

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REFERENCES

1. Anthoni, U., Larsen, Ch. and Nielsen, P. H. *Acta Chem. Scand.* **20** (1966) 1714.
2. Podgornaya, I. V., Tayusheva, N. N. and Postovskii, I. Ya. *Zh. Obshch. Khim.* **34** (1964) 2521.
3. Beckett, T. and Dyson, G. M. *J. Chem. Soc.* **1937** 1358.
4. Caldow, G. L. and Thompson, H. W. *Spectrochim. Acta* **13** (1958) 212.
5. Kjær, A., Ohashi, M., Wilson, J. M. and Djerassi, C. *Acta Chem. Scand.* **17** (1963) 2143.
6. Jensen, K. A., Holm, A., Wentrup, C. and Møller, J. *Acta Chem. Scand.* **20** (1966) 2107.
7. Gilman, H., Honeycutt, Jr., J. B. and Ingman, R. K. *J. Org. Chem.* **22** (1957) 338.
8. Anthoni, U. *Acta Chem. Scand.* **20** (1966) 2742.
9. Ham, N. S. and Willis, J. B. *Spectrochim. Acta* **16** (1960) 279.
10. Tarbell, D. S. and Harnish, D. P. *Chem. Rev.* **49** (1951) 1, 77.
11. Riehmschneider, R., Wojahn, F. and Orlick, G. *J. Am. Chem. Soc.* **73** (1951) 5905.
12. Gardner, W. H. and Weinberger, H. *Inorg. Syn.* **I** (1939) 84.
13. Söderbäck, E. *Ann.* **419** (1919) 217, 276.
14. Kaufmann, H. P. and Oehring, W. *Ber.* **59** (1926) 187.
15. Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 2nd. Ed., Methuen, London 1960.
16. Staab, H. A. and Walther, G. *Ann.* **657** (1962) 98.
17. Marckwald, W. *Ber.* **25** (1892) 3098, 3113.
18. Stahel, R. *Ann.* **258** (1890) 242.

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