

N-Isothiocyanatoamines

IV. Dimerization of *N*-Isothiocyanatodimethylamine

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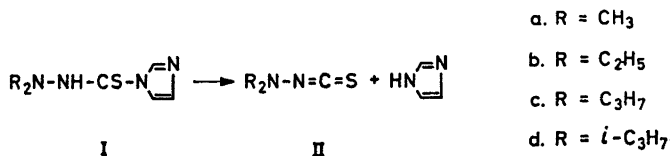
The dimerization of *N*-isothiocyanatodimethylamine has been investigated. The reaction proceeds through a linear dimer which is too unstable to be isolated but has been observed in solution. Two different crystalline dimers have been isolated and shown to be triazole derivatives. The more stable of these, 4-dimethylamino-1-methyl-3-methylthio-1,2,4-triazol-2-ine-5-thione, has been synthesized by an independent route. The possible use of the lead(II) salt of *N,N*-dimethyldithiocarbamic acid as a precursor of *N*-isothiocyanatodimethylamine is briefly discussed.

The dimerization of various compounds containing the $-N=C=X$ group ($X = O, S$) has been the subject of several recent investigations. Generalizations regarding the mechanism of these dimerizations do not seem to be amply justified at this time, but a rather simple picture appears if the dimers are classified according to the size of the rings formed. Dimers containing four-membered rings arise from addition reactions involving the cumulated bond system only. Buckles and McGrew¹ reported evidence for the existence of a highly ordered transition state in the phosphine-catalyzed dimerization of phenyl isocyanate to 1,3-diphenyl-1,3-diazetidone-2,4-dione, *i.e.* dimerization across the $C=N$ double bond. Dimerization of trifluoromethylsulfenyl isocyanate² in the absence of added catalyst gives a corresponding product. On the other hand, Dickoré and Kühle³ have shown that sulfonyl isothiocyanates dimerize exclusively at the $C=S$ double bond to give 1,3-dithietanes. Isothiocyanatoamines according to preliminary data by Staab *et al.*⁴ dimerize with the formation of a four-membered ring. In the case of *N*-isocyanatodimethylamine, however, it has recently been shown that a five-membered ring is formed,⁵ analogous to that discussed in the present paper for *N*-isothiocyanatodimethylamine. Another group of dimers are those arising from compounds in which a double bond such as $C=O$,⁶ $C=S$,⁷ or $C=N$,⁸ is conjugated with the $N=C=X$ group. In such cases six-membered rings are generally

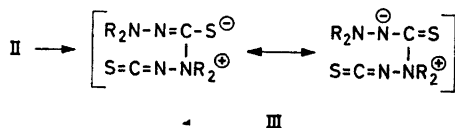
formed. They may conveniently be regarded as originating from Diels-Alder reactions in which the C=N double bond in the N=C=X group of one molecule serves as the dienophile and the conjugated system in another molecule as the diene component. One exception to this rule is the dimerization of methoxythiocarbonyl isocyanate, which may proceed with the formation of a four-membered ring under special circumstances.⁹

We have previously reported¹⁰ that *N*-isothiocyanatodiethylamine (IIb) undergoes spontaneous dimerization at room temperature to a colourless, crystalline product. Experimentally, the elucidation of the structure of this dimer is made difficult by the presence of ethyl groups, which, for example, gives rise to rather complicated mass, infrared, and nuclear magnetic resonance (NMR) spectra. Accordingly, we chose to work primarily with the dimerization of *N*-isothiocyanatodimethylamine (IIa). We wish to report the isolation and characterization of two dimers IVa and Va containing triazole ring systems. The reason for the formation of this unusual ring size is due to the presence of the nucleophilic nitrogen atom next to the NCS group. The mutual support of our results and those reported by Wadsworth and Emmons⁵ for *N*-isocyanatodimethylamine indicates that triazole ring formation is probably quite general for dimerization of >N-N=C=X type compounds.

Pyrolysis in high vacuum¹⁰ of *N,N*-dimethylthiocarbazoylimidazole (Ia), easily accessible from *N,N*-dimethylhydrazine, thiophosgene, and imidazole, gave the required *N*-isothiocyanatodimethylamine monomer (IIa).



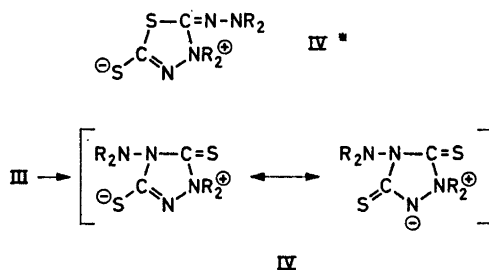
Dimerization of IIa proceeded at a negligible rate at -80°C, but was complete in a minute at room temperature. Comparable results were obtained with IIb and IIc. In marked contrast with this behaviour, samples of *N*-isothiocyanatodiisopropylamine (IIc) needed several hours for dimerization at room temperature,¹¹ and less than 10 % dimerization was observed for dilute solutions of IIc in, *e.g.*, CCl₄ and CHCl₃ after four days at room temperature. The exceptionally high stability of this monomer can be accounted for only in terms of a steric effect. Assuming a common mechanistic pattern beneath these dimerizations, the following representation would account for the observed rates.



The observation that IIc appears to represent the limiting case for the rapid formation of a dimeric species is analogous to the data given by Hünig and Kiessel¹² for the failure of ethyldiisopropylamine to quaternize with

alkyl halides. Moreover, addition compounds of amines and phosphines with isocyanates and isothiocyanates have been isolated and assigned^{1,13} dipolar structures analogous to III. A similar intermediate was suggested recently⁵ for dimerization of *N*-isocyanatodimethylamine. It should be noted that III only is a proposed intermediate in the dimerization reaction and has not been isolated. (Observation by NMR spectroscopy at a later stage, see below). On being allowed to warm to room temperature, IIa formed a product easily separated into two crystalline, colourless compounds, a pentane-insoluble dimer (IVa) and a pentane-soluble dimer (Va).

Structure of IVa. For investigating the structure of IVa a combination of NMR and infrared spectroscopy appeared informative. On recording the NMR spectrum at 60 Mc/sec in methylene chloride, two methyl proton signals of equal intensity were observed with $\tau = 7.18$ ppm and 6.47 ppm. The former peak implies the presence of a dimethylamino group with free rotation about the neighbouring nitrogen-nitrogen bond.¹⁴ We interpret the reduced shielding of the hydrogen atoms of the other dimethylamino group as due to quaternization, *i.e.* we propose a dipolar structure for IVa. It is therefore reasonable to suppose IIIa to cyclize in a fashion involving electrophilic attack of the carbon atom in the $-\text{N}=\text{C}=\text{S}$ group either on the nitrogen or on the sulfur atom, both negatively charged in IIIa, *viz.*

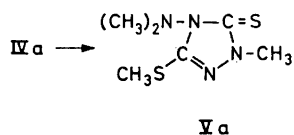


We shall show later that the triazole structure (IV) is in fact most probable. A corresponding structure was proposed for dimeric *N*-isocyanatodimethylamine on the basis of NMR and hydrolysis experiments,⁵ but the possibility of a corresponding dipolar oxadiazole structure for this compound was not considered by Wadsworth and Emmons. Since 1,3,4-thiadiazoles are much more stable than their oxygen analogues, the possibility of IVa having the former structure (IV*) cannot, in the present case, be excluded *a priori*.

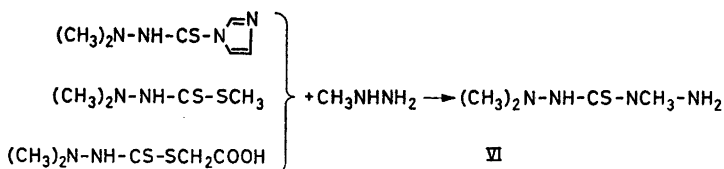
Further information on the structure of IVa was provided by the striking changes observed in the infrared and NMR spectra of IVa on standing in solution at room temperature. According to the infrared spectrum, an essentially complete transformation took place during 2 h. In KBr or CH_2Cl_2 , fresh material showed a series of characteristic absorptions at 625 cm^{-1} (s), 882 cm^{-1} (s), 1024 cm^{-1} (vs), and 1447 cm^{-1} (vs). The first, third, and fourth of these bands are indicative of the presence of a tertiary thioureide grouping,¹⁵ being the G, D, and B band, respectively. In agreement with this, the transformed material showed none of those bands, but instead a broad, very strong

absorption at *ca.* 2060 cm^{-1} characteristic of the $\text{N}=\text{C}=\text{S}$ group. Three reasonable explanations exist for these observations: (1) an equilibrium between IVa and the monomeric species (IIa) had been established, (2) the equilibrium $\text{IVa} \rightleftharpoons \text{IIIa}$ had been displaced to the right, or (3) as (2), but followed by migration of, *e.g.*, a methyl group. Investigation of the NMR spectrum during the same transformation made it clear that several steps were involved, but the shifts accompanying the first step definitely pointed to the second or third alternative. Thus, the signal at 6.46 ppm originating from the $(\text{CH}_3)_2\text{N}^+$ moiety remained effectively constant, whilst the signal from the $(\text{CH}_3)_2\text{N}$ protons was shifted 0.3 ppm downfield from its position in a fresh solution of IVa. The intensity relationship (1:1) remained constant. Though the initial reaction therefore is a ring-opening of IVa to IIIa, secondary reactions occur owing to the instability of IIIa, as indicated by the rapid appearance of several signals with low intensity in addition to the two signals mentioned above. In our opinion, though, this cannot seriously affect the main conclusion, but merely indicates that alternative (3), rather than (2), is correct.

Identification of Va. The pentane-soluble dimer (Va) showed an infrared spectrum devoid of absorption in the region 1500–2900 cm^{-1} and unchanged with time. It was stable to acid and base hydrolysis, but afforded a methiodide with methyl iodide. It was rather unexpected that the basicity of the *N*-dimethylamino group was too small to allow formation of a hydrochloride with concentrated hydrochloric acid, but similar instances are known.⁵ The NMR spectrum in CCl_4 consisted of three singlets at $\tau = 7.50$ ppm ($\text{S}-\text{CH}_3$), $\tau = 6.82$ ppm ($\text{N}(\text{CH}_3)_2$), and $\tau = 6.31$ ppm ($\text{N}-\text{CH}_3$) in the intensity ratios 1:2:1. Consistently with the above scheme, Va could be formulated as arising from an intramolecular rearrangement of a methyl group in IVa without preliminary ring-opening. In fact, experiments showed that IVa could easily be converted to Va by melting or by standing in solution in a glass vessel. On the other hand, Va might also be formed directly from IIa, but no direct evidence can be presented to clarify this point.



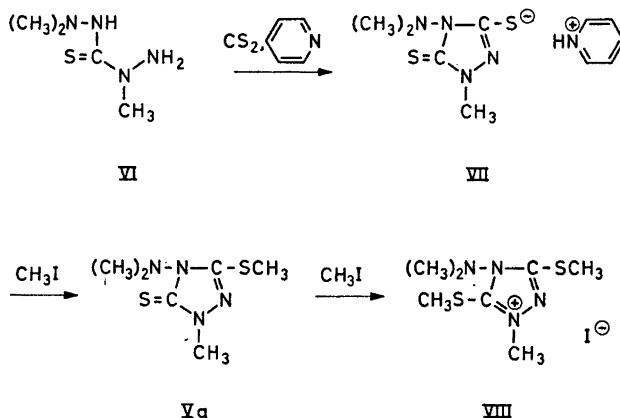
To prove the structure of Va, an independent synthesis now became desirable. The success was of importance also as a means of providing further evidence of the suggested intermediates IIIa and IVa. Initial experiments aiming at the direct joining of an *N,N*-dimethyldithiocarbazic ester with a monomethylthiocarbazic acid derivative were unsuccessful. We next turned to the problem of synthesizing one of the partial skeletons *S*-methyl-1,1,5-trimethylisothiocarbohydrazide (*e.g.* as hydriodide) or 1,1,4-trimethylthiocarbohydrazide (VI). Compounds of these types have not been described. The latter alternative was chosen as the most attractive and turned out to be readily feasible *via* three different routes.



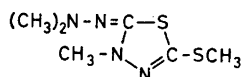
The use of *N,N*-dimethylthiocarbazoylimidazole is an obvious extension of the reaction of such compounds with amines to form thiosemicarbazides.¹⁶ The second method was reported by Sandström¹⁷ for the preparation of thiocarbohydrazide. The third method parallels that used by Jensen¹⁸ for the preparation of thiosemicarbazides, (*cf.* also Brown *et al.*¹⁹). By analogy with extensive work on the preparation of 2-alkylthiosemicarbazides,²⁰ the formation of the isomeric 1,1,5-trimethylthiocarbohydrazide appeared to be precluded. The identity of VI was confirmed by the presence of the highly characteristic NH_2 band (1650 cm^{-1}) and B band (1520 cm^{-1})¹⁵ in the infrared spectrum.

To complete the synthesis of Va a *S*-methylthiocarbonyl group should be introduced to bridge the nitrogen atoms 2 and 5 in VI. Experiments showed that VI is extremely sensitive to acidic compounds such as thiophosgene. Trithiocarbonic esters could not be made to react even on prolonged reflux. Introduction of an *N*-methylthiocarbamoyl group in VI was readily accomplished with methyl isothiocyanate. However, the 1,1,4-trimethyl-5-(*N*-methylthiocarbamoyl)thiocarbohydrazide produced lost *N,N*-dimethylhydrazine with formation of a thiadiazole on treatment with concentrated hydrochloric acid,²¹ instead of cyclizing to a triazole by elimination of methylamine. Cyclization of VI to VII was finally affected by refluxing with carbon disulfide and pyridine as described by Sandström.²² Subsequent treatment of the pyridinium salt (VII) with methyl iodide gave authentic Va.

An additional possibility exists for the structure of the compound obtained from VI by this sequence of reactions, namely the thiadiazole IX. Special



care was taken to exclude this possibility since it was realized that the same compound would be formed from IV* by migration of a methyl group. The exclusion of the structure IX thus at the same time supports the structure of IV.

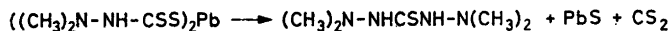


IX

The proof was derived from the fact that when Va was treated with methyl iodide, the product (VIII) exhibited two S—CH₃ peaks close together in the NMR spectrum. This was confirmed by deuteration (using methyl-*d*₃ iodide). If the thiadiazole structure (IX) had been correct, the methiodide derived from it could not have had the same characteristics. Even if methylation should occur on the heterocyclic sulfur atom, the resultant S⁺—CH₃ peak would be widely separated from the signal arising from the S—CH₃ group.*

After the structures of these dimers were clarified, the pentane-insoluble higher homologues IVb,¹⁰ IVc, and IVd¹¹ were investigated. These results as well as mass spectroscopic studies on the compounds involved in the present study will be published in subsequent articles, but we should like to mention two interesting observations in this connection. First, IVb—IVd all seem to undergo initial ring-fission to IIIb—IIIc in solution, but the diisopropyl dimer (IVd) has the lowest rate. This shows that ring opening is probably controlled by other than steric factors. Second, the formation of compounds analogous to Va has not been observed with higher homologues.

Pyrolysis of carbazic esters have been shown to produce dimeric *N*-isocyanatoamines.⁵ We found that thermolysis of bis-(*N,N*-dimethyldithiocarbazato)-lead(II) in boiling hexane in the same way afforded Va, whilst using boiling toluene gave instead 1,1,5,5-tetramethylthiocarbohydrazide (X).



X

EXPERIMENTAL

Conditions and equipment used for the physical measurements were those described in part II of this series.^{1a}

1-(N,N-Dimethylthiocarbazoyl)-imidazole (Ia). Imidazole (0.1 mole) was dissolved in chloroform (50 ml) previously distilled over P₂O₅. Thiophosgene (0.025 mole) dissolved

* *Note added in proof.* The reaction sequence VI → VII → Va → VIII has been repeated with thiocarbonylthiohydrazide instead of VI. The compounds thus prepared have been shown by Sandström²² to be 1,2,4-triazoles and not thiadiazoles. Comparison of the IR and NMR spectra of these triazoles to those of VII, Va and VIII substantiated the formulation of the latter compounds as triazoles rather than thiadiazoles. The details of this investigation will be published later.

in dry benzene (20 ml) was added at room temperature, with stirring, to the solution and stirring was continued at room temperature for $\frac{1}{2}$ h. The solution was cooled to 0°C and the imidazolium chloride was filtered off and washed once with dry benzene. The combined filtrate and washings were stirred as *N,N*-dimethylhydrazine (0.025 mole) dissolved in dry benzene (20 ml) was added dropwise at room temperature during $\frac{1}{2}$ h. Stirring was continued for another $\frac{1}{2}$ h. The reaction mixture was taken to dryness *in vacuo*, allowed to crystallize (important), and digested 3 times with 50-ml portions of boiling ether to remove the imidazole. The residue (90 % yield) could be recrystallized with great loss to give colourless crystals (Ia), m.p. 128–129°C. (Found: C 42.12; H 5.82. Calc. for $C_6H_{10}N_4S$: C 42.33; H 5.92). The infrared spectrum was consistent with the proposed structure.

Thermolysis of Ia in methanol. A solution of Ia (5 g) in methanol (75 ml) was refluxed for some time. (If the crude product from the above preparation was used, 1 h was sufficient to effect complete reaction. For highly purified samples it was necessary to maintain reflux for 2–5 additional hours). The methanol was removed at reduced pressure and the residual solid freed from imidazole by extraction with cold water. Recrystallization from water or pentane afforded colourless crystals in 30 % yield; m.p. 126–127°C. The product was shown to be *4-dimethylamino-1-methyl-3-methylthio-1,2,4-triazol-2-ine-5-thione* (Va) by m.p., mixture m.p., and identity in infrared spectrum with an authentic sample (see below). (Found: C 35.22; H 5.56; S 31.10. Calc. for $C_6H_{12}N_4S_2$: C 35.27; H 5.92; S 31.38). The molecular weight was determined by mass spectroscopy.

IR-spectrum (KBr, in cm^{-1}): 2992w, 2967w, 2939w, 2900w, 1495s, 1458m, 1440s, 1423w, 1382vs, 1352w, 1322s, 1210m, 1162w, 1146w, 1066m, 1020w, 995w, 980m, 925w, 806s, 684w, 636w, 598w, 553w.

Thermolysis of Ia in high vacuum. The apparatus used was essentially that described earlier¹⁰ for preparation of *N*-isothiocyanatodiethylamine. To prevent sublimation of Ia in the receiver, it was found advantageous to extend the air-cooled part of the glass tube *ca.* 100 cm. The glass tube was charged with Ia (300 mg) spread evenly over the bottom of the reaction chamber. In order to ensure maximum decomposition of the subliming Ia, a loose plug of platinum gauze was inserted in the outer end of the reaction chamber and heated separately with a split furnace to *ca.* 125°C. During the thermolysis — which could easily be followed and controlled by the appearance of imidazole and sublimed Ia in the unheated part of the glass tube — the pressure was held between 10^{-3} and 10^{-4} mm Hg. After $\frac{1}{2}$ h of heating, only small amounts of a brownish oil were left in the heated part of the glass tube and yellowish crystals (20–80 mg) of monomeric *N*-isothiocyanatodimethylamine (IIa) had collected in the trap cooled in liquid air. Attempts to determine the m.p. were unsuccessful due to the extreme tendency to dimerize, but the observation that the yellow oil formed on melting IIa resolidified almost instantly with formation of dimerized material supported the proposed structure. When IIa was treated with ethanolic aniline at low temperature, *1,1-dimethyl-4-phenylthiosemicarbazide*, identical by infrared spectrum and m.p. with an authentic specimen, was formed. The same reaction does not proceed with any of the dimers IVa or Va, thus supporting IIa as the monomer.

The crude dimerized material was extracted several times with pentane. Evaporation of the combined pentane extracts to dryness *in vacuo* afforded 25–40 mg of crystalline material, which was recrystallized from water to give colourless crystals, shown by m.p., mixture m.p., and infrared spectroscopy to be Va, identical with the product obtained by heating Ia in ethanol.

The colourless, crystalline *pentane-insoluble dimer* (IVa) left by this extraction melts between 82 and 88°C with almost exclusive rearrangement to Va. The molecular weight was determined by mass spectroscopy. (Found: C 35.36; H 5.77; N 27.32. Calc. for $C_6H_{12}N_4S_2$: C 35.27; H 5.92; N 27.43). IR-spectrum (KBr, in cm^{-1}): 3035w, 3020m, 2990w, 2962m, 2900w, 2879m, 2836w, 2790w, 1628m, 1460s, 1447vs, 1428vs, 1355vw, 1300vw, 1256w, 1207m, 1152vw, 1084w, 1047m, 1024vs, 995s, 968m, 882s, 848w, 808w, 704w, 652vw, 625s, 594w, 546m, 490w, 447w. Dry, crystalline IVa did not alter significantly in melting point or infrared spectrum on standing for a week. Once it was pressed into a KBr disc or dissolved in methylene chloride, however, a rapid transformation took place. When the methylene chloride solution was placed in a glass vessel, the reaction proceeded at a low rate. When it was followed on the NMR spectrograph, the ap-

pearance of three signals characteristic of Va was observed. Since treatment of IVa with ethereal ammonia gave Va in quantitative yield, considering the rearrangement to be described, we attribute the preceding rearrangement to catalysis by base from the glass. The rearrangement of the same methylene chloride solution in a sodium chloride cell or of IVa pressed in a potassium bromide disc proceeded at a much higher rate and was easily followed in the infrared spectrum by the appearance of a strong absorption at 2060 cm^{-1} . A plot of the intensity of this absorption *versus* time indicates that the reaction (ring opening) is not a simple first or second order reaction. The 2060 cm^{-1} absorption reached a maximum value in 2 h, and only small changes in the spectrum were observed during the next 24 h. When the methylene chloride was removed from the rearranged solution *in vacuo*, the remaining yellow oil proved to be very unstable. Attempted purification was unsuccessful, but the mass spectrum indicated that a mixture of two compounds with molecular weights corresponding to dimers was present in the oil.

1,1,4-Trimethylthiocarbohydrazide (VI). Method a. To a solution of Ia (3.2 g) in absolute ethanol (5 ml) was added methylhydrazine (1 g) and the reaction mixture was allowed to stand for a week at room temperature. Evaporation of the solvent and recrystallization from ethanol gave a 56 % yield of colourless crystalline VI, m.p. $150-151^{\circ}\text{C}$. On prolonged standing of VI a red colour develops, analogous to the behaviour of 4,4-dialkylthiosemicarbazides.²³ (Found: C 32.60; H 8.34; N 37.65; S 21.42. Calc. for $\text{C}_6\text{H}_{12}\text{N}_4\text{S}$: C 32.41; H 8.16; N 37.80; S 21.63). The most important evidence that the compound is not 1,1,5-trimethylthiocarbohydrazide is a band in the infrared spectrum at 1650 cm^{-1} (s), which was confirmed by deuteration to be due to the NH_2 deformation vibration. *Method b.* Methyl *N,N*-dimethyldithiocarbamate¹⁷ was boiled for $\frac{1}{2}$ h with a slight excess of methylhydrazine. The methylhydrazine was removed in vacuum and the remaining solid recrystallized from ethanol to give a 85 % yield of VI. *Method c.* Carboxymethyl *N,N*-dimethyldithiocarbamate (6 g)¹⁹ was boiled for 15 min with methylhydrazine (2.5 g) in water (1.5 ml). On cooling, VI separated in 38 % yield. On evaporation of the mother liquor a substantial additional yield could be obtained. The identity of the products obtained by these three methods was confirmed by mixture m.p. and infrared spectrum.

1,1,4-Trimethyl-5-(N-methylthiocarbamoyl)thiocarbohydrazide. To a solution of VI (6 g) in ethanol at reflux temperature, methyl isothiocyanate (3 g) was added. When a crystalline product began to separate from the boiling solution, it was cooled and filtered. The crude product (90 % yield) was recrystallized from water to give colourless crystals, m.p. $176-177^{\circ}\text{C}$. (Found: C 32.48; H 6.93; N 31.52; S 28.71. Calc. for $\text{C}_6\text{H}_{15}\text{N}_5\text{S}_2$: C 32.55; H 6.83; N 31.65; S 28.97). In accordance with the assigned structure, the infrared spectrum showed no NH_2 band in the $1600-1700\text{ cm}^{-1}$ region, but a double B band¹⁵ at 1550 cm^{-1} (vs) and 1530 cm^{-1} (vs).

2-Methylimino-4-methyl-1,3,4-thiadiazolidine-5-thione. 1,1,4-Trimethyl-5-(*N*-methylthiocarbamoyl)thiocarbohydrazide was boiled with concentrated hydrochloric acid for $\frac{1}{4}$ h. The solution was carefully neutralized and the solvent evaporated. The residue was taken up in ethanol and recrystallized to give a 15 % yield of colourless crystals, m.p. $185-186^{\circ}\text{C}$. (Found: C 29.68; H 4.45; N 26.04. Calc. for $\text{C}_4\text{H}_7\text{N}_3\text{S}_2$: C 29.79; H 4.38; N 26.07). The NMR spectrum in dimethylsulfoxide- d_6 shows two $\text{N}-\text{CH}_3$ signals at $\tau = 7.09$ ppm and 6.50 ppm with equal intensity. In the infrared spectrum no absorption due to $\text{S}-\text{H}$ stretching could be detected, but on deuteration a very strong ND stretching band was observed at 2260 cm^{-1} and a strong, very broad band at *ca.* 2850 cm^{-1} , originating from a NH stretching vibration, disappeared. In view of the close similarity between the structures of the 1,4-dimethyl-1,2,4-triazolidine-3,5-dithione, which might have been formed instead by the above reaction, and XI reported below, a triazolidine structure appears excluded by this observation as well as by the considerable overall difference between the infrared spectra. This is a rather unexpected result, since Guha and De²¹ have reported 1-thiocarbamoylthiocarbohydrazide to form 4-amino-1,2,4-triazolidine-3,5-dithione by an identical reaction.

Pyridinium salt (VII) of 4-dimethylamino-3-mercapto-1-methyl-1,2,4-triazol-2-ine-5-thione (XI). A solution of VI (3.0 g) and carbon disulfide (3.0 g) in pyridine (40 ml) was boiled for $1\frac{1}{2}$ h. After removal of the excess pyridine *in vacuo*, a nearly quantitative yield of VII separated as yellow crystals. These were purified by dissolving them in water and filtering off a yellow insoluble substance (m.p. $128-129^{\circ}\text{C}$, yield 0.5 %, identified as the *disulfide* of XI by an infrared spectrum nearly superposable on that of XI minus the SH stretching vibration). The aqueous solution was then freed of a yellow contaminant

by extraction with ether, and finally addition of hydrochloric acid precipitated *pure XI*, m.p. 75–76°C. (Found: C 31.61; H 5.49; N 29.20; S 33.65. Calc. for $C_5H_{10}N_4S_2$: C 31.56; H 5.30; N 29.45; S 33.70). The NMR spectrum of XI in $CDCl_3$ displays three singlets at $\tau = 6.79$ ppm ($N(CH_3)_2$), 6.35 ppm ($N-CH_3$), and 5.33 ppm (SH , rather broad) in the correct intensity ratio. The infrared spectrum of XI showed a close resemblance to that of Va, and indeed a band with medium strength at 2530 cm^{-1} indicates a thiol structure for XI. The reason for this structure is probably that it allows XI to achieve hetero-aromatic character by simultaneously adopting a dipolar structure $>N-C=S \longleftrightarrow$,

$>N^+=C-S^-$. When XI is dissolved in anhydrous ether and dry pyridine is added,

bright yellow crystals of *pure VII*, m.p. 115–116°C (recovery 95 %) are formed. (Found C 44.80; H 5.77; N 26.20; S 23.75. Calc. for $C_{10}H_{16}N_5S_2$: C 44.58; H 5.61; N 26.00; S 23.80).

Conversion of VII to Va and VIII. To a suspension of VII (0.25 g) in absolute ethanol (5 ml) was added a slight excess of methyl iodide. The mixture was heated to the boiling point for a short time, cooled, and evaporated to dryness. Recrystallization from water followed by pentane furnished a 90 % yield of Va, identical with the product obtained by thermolysis of Ia in ethanol. By treatment of Va with an excess of methyl iodide, a crystalline product separated which was filtered off and washed with ether and pentane. A nearly quantitative yield of *pure VIII*, m.p. 139–141°C, was obtained as colourless crystals. (Found: C 24.14; H 4.41; I 36.94; N 16.23. Calc. for $C_7H_{15}IN_4S_2$: C 24.29; H 4.37; I 36.65; N 16.18). The NMR spectrum compared to that of Va reflects the changes induced by introducing a positive charge in the heterocyclic ring. The $N-CH_3$ signal is shifted from $\tau = 6.31$ ppm in Va to 5.96 ppm, whilst the $N(CH_3)_2$ signal is nearly unaltered ($\tau = 6.90$ ppm). Two $S-CH_3$ signals are observed. The signal at $\tau = 7.29$ ppm arises from the $CH_3S-C=N-$ moiety, whilst the signal at 7.25 ppm originates

from the $CH_3S-C=N^+$ grouping. In accordance with this, the latter signal disappears if methyl iodide- d_3 is used in the conversion of Va to VIII.

Pyrolysis of bis-(N,N-dimethyldithiocarbazato)-lead(II). This was prepared in analogous way to the nickel(II) salt described previously,²⁴ using lead(II) acetate. If it is boiled with hexane for 2 h, and the hexane solution is filtered and evaporated to dryness, the dimer (Va) is isolated. This was characterized by mixture m.p. and infrared spectral comparison with authentic material. Thermolysis at 100–110°C (*i.e.* either by heating on the steam bath or by reflux with toluene) instead afforded a colourless, crystalline product melting at 162–163°C. This was identified as 1,1,5,5-tetramethylthiocarbonylhydrazide by analysis, infrared spectrum and NMR spectrum. The latter showed only one peak at $\tau = 7.39$ ppm in $CDCl_3$. (Found: C 37.05; H 8.48; N 34.46. Calc. for $C_8H_{14}N_4S$: C 37.01; H 8.70; N 34.54).

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