

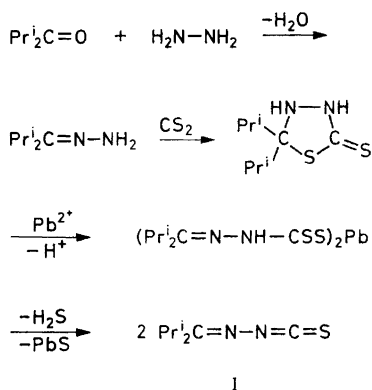
## *N*-Isothiocyanatoimines

### I. On the Preparation and Structure of *N*-Isothiocyanato-2,4-dimethyl-3-pentanimine

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In connection with studies of compounds containing the  $>N-N=C=S$  grouping<sup>1ab</sup> (*N*-Isothiocyanatoamines), the possible extension of the work to compounds of the type  $>C=N-N=C=S$  (*N*-Isothiocyanatoimines) became of interest. This would allow an investigation of the influence of the  $C=N$  double bond on the reactivity and geometry of the  $N=C=S$  system. From earlier experiments with *N*-isothiocyanatoamines<sup>1c,2</sup> it was deduced that a pyrolytic method might be suitable for the synthesis of *N*-isothiocyanatoimines. The present paper reports the thermal degradation of lead bis[3-(diisopropylmethylene)dithiocarbazate] to *N*-isothiocyanato-2,4-dimethyl-3-pentanimine (I). The full reaction sequence leading to (I) is outlined below.

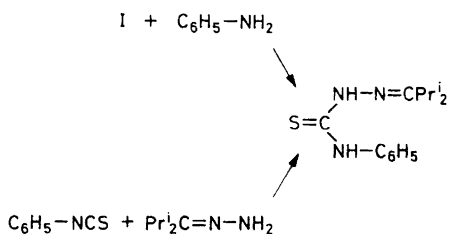


The reaction between various substituted hydrazones and carbon disulfide, leading to 5,5-dialkyl-1,3,4-thiadiazolidine-2-thiones, has recently been described by Heugebaert and Willems.<sup>3</sup> The ring open-

ing of these compounds, into salts and esters of alkylidenedithiocarbazic acids, has lately been investigated by us.<sup>4</sup>

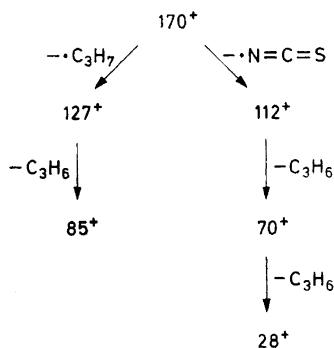
Monomeric (I) is a red-yellow oil which, as expected,<sup>1c,5</sup> readily dimerizes on standing at room temperature. The structure assigned to (I) is based upon the chemical and physical evidence presented here; the structure of the dimer, however, is still under investigation.

Reaction of (I) with aniline yields diisopropylketone-4-phenylthiosemicarbazone, which was shown to be identical with an authentic sample, prepared from diisopropylketonehydrazone and phenylisothiocyanate, by both a comparison of their IR spectra and by mixture melting points.



If rearrangements do not occur, this result provides definite proof of the structure of (I).

The mass spectrum of (I) showed the molecular weight to be 170, and no trace of the dimer could be detected. The main fragmentation paths are schematically:

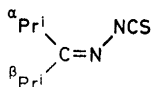


The molecular ion is of appreciable intensity, and the main fragmentation path probably proceeds through loss of an isopropyl radical, to give  $\text{C}_3\text{H}_7\text{C}\equiv\text{N}^+$

$\text{N}=\text{C}=\text{S}$  ( $m/e$  127), with subsequent elimination of propylene to yield  $\text{H}-\text{C}\equiv\overset{+}{\text{N}}-\text{N}=\text{C}=\text{S}$  ( $m/e$  85). An alternative route for the degradation is loss of the NCS radical to give  $(\text{C}_3\text{H}_7)_2\text{C}=\overset{+}{\text{N}}$  ( $m/e$  112), followed by elimination of propylene yielding  $(\text{CH}_3)_2\text{CH}-\text{C}\equiv\overset{+}{\text{N}}\text{H}$  ( $m/e$  70) and, finally, expulsion of another molecule of propylene to form  $\text{H}-\text{C}\equiv\overset{+}{\text{N}}\text{H}$  ( $m/e$  28).

The mass spectrum of (I) exhibits only a few fragmentation patterns analogous to those reported for *N*-isothiocyanatodiisopropylamine.<sup>6</sup> Further, the loss of sulfur, which is one of the important degradation ways for the latter compound, is not observed in the mass spectrum of (I). This may be partially accounted for by the different conditions under which the spectra were obtained.

The  $^1\text{H}$  NMR spectrum of (I) would be expected to exhibit two septuplets and two doublets when the isopropyl groups are anisochronous.\*



Alternatively, in the case of rapid inversion at the nitrogen atom, one septuplet and one doublet would be expected. When the spectrum was recorded in  $\text{CD}_3\text{OD}$  at  $-30^\circ\text{C}$ , two septuplets (centred at  $\tau=6.89$  ppm and  $\tau=7.33$  ppm) and two doublets (centred at  $\tau=8.76$  ppm and  $\tau=8.88$  ppm) were observed. Similarly when the  $^1\text{H}$  NMR spectrum of (I) was recorded in  $\text{CDCl}_3$  at  $-30^\circ\text{C}$ , two septuplets (centred at  $\tau=6.66$  ppm and  $\tau=7.24$  ppm) were observed for the methine protons. The six methyl protons appeared, however, as one doublet centred at  $\tau=8.84$  ppm with a spacing of 7.0 Hz, identical with the spacing found in the septuplet. The only explanation of the failure to detect two doublets in the  $^1\text{H}$  NMR spectrum of (I), in  $\text{CDCl}_3$ , is to assume that an accidental coincidence of the two methyl proton signals occurs.

\* This term is used (Shvo, Y., Taylor, E. C., Mislow, K. and Raban, M. *J. Am. Chem. Soc.* 89 (1967) 4910) to signify "magnetically nonequivalent, in the chemical shift sense".

The IR spectrum of (I) in  $\text{CHCl}_3$  was decisive in establishing the presence of the isothiocyanate grouping, which produces a broad and very strong band centred around  $2100\text{ cm}^{-1}$ . This band exhibits a highly characteristic shape; it is found in all organic isothiocyanates,<sup>7</sup> and it is due mainly to the antisymmetric stretching vibration of the  $\text{N}=\text{C}=\text{S}$  group. It is always accompanied by another band, of low intensity, at a higher wavenumber.<sup>7,8</sup> These two "NCS bands" are found at  $2125\text{ cm}^{-1}$  (w,sh) and at  $2035\text{ cm}^{-1}$  (vs) in the IR spectrum of *N*-isothiocyanatodiisopropylamine.<sup>6</sup> In the IR spectrum of (I) they occur at slightly lower wavenumbers *viz* ( $2075\text{ cm}^{-1}$  (m,sh) and  $1980\text{ cm}^{-1}$  (vs); (see experimental part). This displacement towards lower wavenumbers is probably due to electron delocalisation between the  $\text{C}=\text{N}$  bond conjugated with the  $\text{N}=\text{C}=\text{S}$  group.

Further work on this new class of compound will be presented in subsequent papers.

*Experimental.* Microanalyses were carried out in the microanalysis department of this laboratory. Melting points were determined on a Reichert melting point microscope and were not corrected. Conditions and equipment for the IR and  $^1\text{H}$  NMR measurements have been described in an earlier paper.<sup>4</sup> The mass spectra were obtained on a AEI-MS 9 spectrometer using direct insertion of the sample into the ion source. The temperature of the ion source was  $60^\circ\text{C}$ , and the ionizing potential  $70\text{ eV}$ .

*Diisopropylketonehydrazone.* Pearson *et al.*<sup>9</sup> have briefly mentioned the preparation of diisopropylketonehydrazone, but omitted all details of experimentation and characterization.

Diisopropylketone (0.1 mol) and anhydrous hydrazine (0.2 mol) were refluxed for 20 h without solvent. The mixture was distilled *in vacuo*, and the fraction boiling between  $57$  and  $61^\circ\text{C}$  at 7 mm Hg was redistilled. The yield was 50 % with a b.p.  $59-61^\circ\text{C}/7\text{ mm Hg}$ . (Found: C 64.78; H 12.48; N 21.75. Calc. for  $\text{C}_7\text{H}_{16}\text{N}_2$ : C 65.57; H 12.58; N 21.85). Both the IR and  $^1\text{H}$  NMR spectra of this compound were consistent with the structure proposed for diisopropylketonehydrazone.

*5,5-Diisopropyl-1,3,4-thiadiazolidine-2-thione.* This compound was prepared following the directions given in method B for 5,5-dimethyl-1,3,4-thiadiazolidine-2-thione by Heugebaert and Willems.<sup>3</sup> The yield of colourless needles with a m.p.  $114-114.5^\circ\text{C}$  was 75 %. (Found:

C 46.95; H 7.82; N 13.67. Calc. for  $C_8H_{16}N_2S_2$ : C 47.02; H 7.89; N 13.71).

From the IR and  $^1H$  NMR spectra of this compound, it may be concluded that it is a 1,3,4-thiadiazolidine-2-thione, rather than an alkylidenedithiocarbazic acid.<sup>4</sup>

*Lead bis[3-(diisopropylmethylene)dithiocarbazate]*. An equimolar amount of lead(II) acetate in water (10 ml) was slowly added to a stirred solution of 5,5-diisopropyl-1,3,4-thiadiazolidine-2-thione (1 g) in methanol-water (80 ml; 1:1). The crystalline precipitate of yellow lead(II) salt was filtered off, washed with water (50 ml), and finally dried for 24 h over sulfuric acid *in vacuo*. The yield was almost quantitative, and the crude material was used without further purification for the next step.

*N-Isothiocyanato-2,4-dimethyl-3-pentanimine monomer (I)*. The apparatus and the procedure described for the preparation of *N*-isothiocyanatodiethylamine<sup>12</sup> proved convenient with a few modifications. The heating was performed with an electric heating mantle kept at 120°C. The receiver was cooled with a methanol/ice bath to only -15°C. In this way the condensation of hydrogen sulfide, formed by the pyrolysis, was avoided. The yield of red-yellow (I) was in the range 50–60%. The melting point was *ca.* -120°C. (Found: C 56.35; H 9.23; N 16.37. Calc. for  $C_8H_{14}N_2S$ : C 56.43; H 8.29; N 16.45). The molecular weight was shown by mass spectrometry to be 170 (see text).

The IR spectrum in  $CHCl_3$  showed the following characteristic bands (in  $cm^{-1}$ ): 2965s, 2925m, 2835w, 2325w, 2075m (sh); 1980vs, 1475m, 1018s, 902m, 654m.

Although complete dimerization of (I) takes place within 15 min upon standing at room temperature, it can be stored in liquid air under nitrogen. (I) is moderately stable when dissolved in an inert solvent such as  $CHCl_3$  or  $CCl_4$ . It was determined, from the  $^1H$  NMR spectrum that (I) was approximately 20% dimerized in a 5%  $CDCl_3$  solution after standing for 4 h at room temperature.

*N-Isothiocyanato-2,4-dimethyl-3-pentanimine dimer*. When (I) was allowed to stand at room temperature it crystallized within 15 min. The light yellow microcrystalline substance had a melting point at 124–125°C, and was shown by mass spectrometry to correspond to a dimer of (I), which a molecular weight of  $M=340$ . (Found: C 56.20; H 8.11; N 16.46. Calc. for  $C_{16}H_{28}N_4S_2$ : C 56.43; H 8.29; N 16.45).

The IR spectrum in KBr showed the following characteristic bands (in  $cm^{-1}$ ): 1970m, 1935w, 1870vw, 1520s, 1400s, 1245m, 1022m, 987s.

*Diisopropylketone-4-phenylthiosemicarbazone.*

A slight excess of aniline was added dropwise to (I) (200 mg), cooled in liquid air. When the reaction mixture was warmed to room temperature, crystals were formed, which were washed with water and recrystallized from ethanol. A 40% yield of a colourless crystalline compound (m.p. 90–91°C) was obtained. (Found: C 63.61; H 7.90; N 15.96. Calc. for  $C_{14}H_{21}N_3S$ : C 63.85; H 8.04; N 15.95).

An authentic sample of diisopropylketone-4-phenylthiosemicarbazone was prepared in the following way: Phenylisothiocyanate (0.4 g), in dry ether (5 ml), was added over a period of 5 min to a stirred solution of freshly prepared diisopropylketonehydrazone (0.4 g) dissolved in dry ether (10 ml). The stirring was continued for a further 2 h, after which the solution was evaporated to dryness *in vacuo*. The residue was recrystallized from ethanol to give colourless crystals of diisopropylketone-4-phenylthiosemicarbazone with a m.p. 90–91°C; the yield was 35%. The compounds formed in the two different pathways were proved to be identical by their IR spectra and by mixture melting points. The IR and  $^1H$  NMR spectra were consistent with the structure proposed for diisopropylketone-4-phenylthiosemicarbazone. The tautomeric 1,3,4-triazolidine-2-one structure, which has recently been reported for acetone-2-phenylsemicarbazone,<sup>10</sup> can be excluded.

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