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N-Isothiocyanatoamines

III. *N*-Isothiocyanatodiisopropylamine. Preparation, Physical Properties, and Reactions with Amines and Hydrazines

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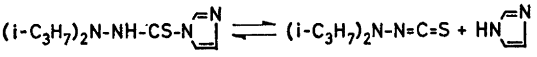
N-Isothiocyanatodiisopropylamine, an unusually stable representative of the class of *N*-isothiocyanatoamines, has been prepared by thermolysis of *N*,*N*-diisopropylthiocarbazoylimidazole in high vacuum. Its IR, NMR, and mass spectra are reported and discussed and its reactions with amines, hydrazines, benzhydrazide, *p*-toluenesulfonohydrazide, 1,3-diphenylguanidine, and 4,4-dimethylthiosemicarbazide have been investigated. It is concluded that the reactivity of *N*-isothiocyanatoamines is generally higher than that of alkyl isothiocyanates.

In part I of this series,[1] a method was devised for preparing *N*-isothiocyanatodiethylamine from 1-(*N*,*N*-diethylthiocarbazoyl)-imidazole by thermolysis in high vacuum. Although stable for several days at −80°C, this compound was not well suited for investigations of the chemistry of *N*-isothiocyanatoamines owing to the pronounced tendency to dimerisation at room temperature. In part II,[2] it was established that *N*-isothiocyanatodiphenylamine was even more unstable, rearranging instantly to 2-thiocyanatodiphenylamine at room temperature.

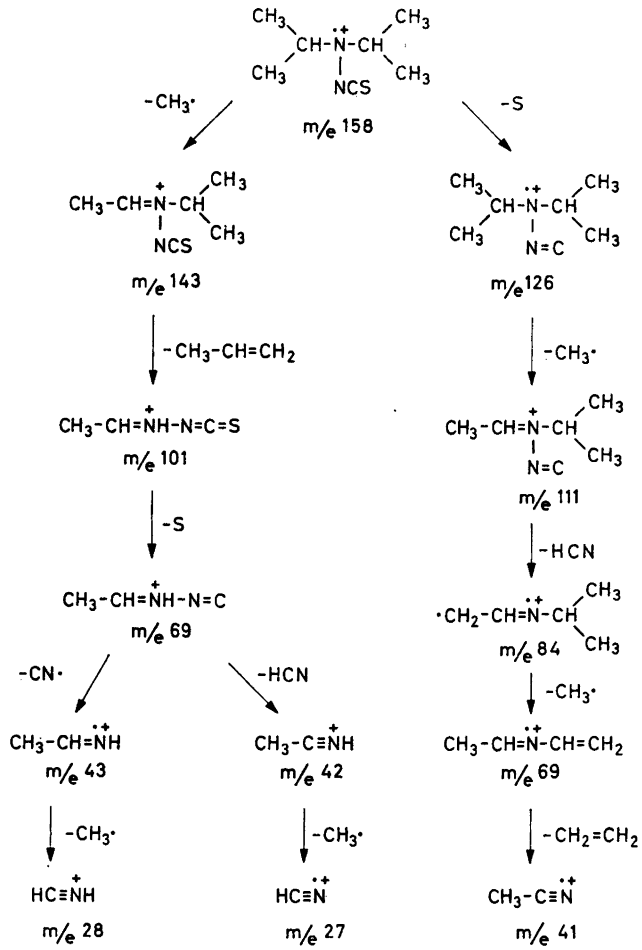
Since simple *N*-isothiocyanatoamines represent a new class of organic compounds several *N*-isothiocyanatodialkylamines were prepared and their stability examined. It was found that *N*-isothiocyanatodiisopropylamine (I) possesses an exceptionally high stability relative to the lower aliphatic analogues. This can only be attributed to the steric effect of the isopropyl groups and suggests that the dimerisation reaction [3] involves interaction of the amino group of one molecule with the isothiocyanate group of another.

The preparation of (I) was accomplished by heating 1-(*N*,*N*-diisopropylthiocarbazoyl)-imidazole *in vacuo*:



The work of Staab *et al.*[4] on the preparation of isocyanates and isothiocyanates by heating *N*-carbamoyl- and *N*-thiocarbamoylimidazoles has made it clear that reactions of this type are generally reversible. Our results show that recombination of (I) with imidazole easily takes place in solution suggesting reversibility also in the present case.

Monomeric (I) is a yellow oil stable for several hours at room temperature. The assigned structure rests upon nuclear magnetic resonance (NMR), infrared (IR), and mass spectroscopic evidence. The NMR spectrum permitted the isopropyl groups to be identified unambiguously, showing the α-proton resonance, centered at $\tau = 6.76$, split into seven, and the resonance of six β-protons, centered at $\tau = 8.83$, split into a doublet. The IR spectrum was equally decisive in establishing the presence of the isothiocyanate grouping. The most important infrared characteristic of this is the band due to the antisymmetric stretching vibration, previously observed at 2040 cm^{-1} (vs) +



2010 cm^{-1} (s) in the spectrum of *N*-isothiocyanatodiethylamine.[1] In accord with this the spectrum of (I), recorded in CS_2 or CCl_4, showed a very strong band at 2035 cm^{-1} with a shoulder at 2125 cm^{-1}.

The position and intensity of the peaks in the mass spectrum are presented in the experimental part. The scheme outlined above illustrates the two most favoured fragmentation patterns of (I). A characteristic feature of each of the three peaks at *m/e* 158, 143, and 101 is the occurrence of two small, but distinct peaks with one and two additional mass units. Calculations based on the formulae proposed for these ions show good agreement with the contents of natural isotopic species. This, together with two metastable peaks observed at about *m/e* 129 and *m/e* 71, indicate the main fragmentation of the molecular ion to proceed through loss of a methyl group followed by expulsion of propene. The two most abundant ions, *m/e* 69 and *m/e* 43, may conceivably be formed by stepwise degradation of the isothiocyanate group. It should be noted that the intensity of the peak at *m/e* 71 definitely excludes that the *m/e* 69 ion contains sulfur in accord with the proposed scheme. In an alternative but less favourable route to the *m/e* 69 ion (illustrated to the right in the scheme) an ion with *m/e* 126 is formed by initial loss of sulfur (intensity of *m/e* 128 peak). The further fragmentation proceeds with loss of a methyl radical (metastable peak at *m/e* 98) and elimination of hydrogen cyanide by a cyclic mechanism followed by expulsion of another methyl group furnishing a vinyliminyl cation at *m/e* 69. Kjær *et al.*[5] have studied the mass spectra of isothiocyanates in detail. They found α- and β-fission to be predominant in the case of lower alkyl isothiocyanates and loss of SH by a cyclic mechanism to be characteristic only for the higher members. In the case of (I), however, fission of the bonds α or β to the N-NCS moiety seems to be equally important. The ready loss of sulfur is a distinguishing feature reflecting the increased tendency for (I) to form the resonance stabilized ions *m/e* 126 and *m/e* 69.

As part of our systematic investigations of the chemistry of *N*-isothiocyanatoamines we present below the results obtained when reacting (I) with compounds containing amine and hydrazine groups. The unique stability of (I) makes it well suited for this purpose and troublesome by-products have only seldom been encountered. Although several competing reactions may be envisioned for *N*-isothiocyanatoamines, the most liable to occur is dimerization. It appears to proceed with comparative ease in diluted, alkaline solutions which have accordingly been avoided when possible. In a communication from this laboratory the preparation of various substituted thiosemicarbazides is reported in detail.[6] An alternative approach to the synthesis of 1,1-dialkylthiosemicarbazides is now offered by the reaction of ammonia and amines with *N*-isothiocyanatodialkylamines, *e.g.*

$$(i\text{-}C_3H_7)_2N-N=C=S + CH_3NH_2 \longrightarrow (i\text{-}C_3H_7)_2N-NH-CS-NH-CH_3$$

The yields obtained in the reaction with ammonia and methylamine (10—20 %) leave much to be desired, but applying the same method to the preparation of 4-phenyl- and ethylene-4,4'-bis-(1,1-diisopropylthiosemicarbazide) resulted in satisfactory yields of pure materials. In a similar manner, reaction of (I) with piperidine, assisted by moderate heating, readily afforded 1,1-diisopropyl-4,4-pentamethylenethiosemicarbazide. The reaction with ethyl-

enediamine deserves special interest in so far as (I) reacts smoothly with *both* amino groups. This observation is difficult to reconcile with the proposal of McElhinney [7] that reactions of dithiocarbazic esters with amines involve NH_2NCS as an intermediate. If so, the reaction with ethylenediamine should give 4,4′-ethylenebisthiosemicarbazide, but in fact only ethylenethiourea, formed from the intermediate 4-(2-aminoethyl)-thiosemicarbazide, was isolated. Moreover, the stability so far observed for *N*-isothiocyanatoamines also makes it unlikely that they would function as intermediates in any high-temperature reactions.

Hydrazine reacts with two molecules of (I) to produce 4,4′-bi(1,1-diisopropylthiosemicarbazide).

$$2(\text{i-}C_3H_7)_2N-N=C=S + NH_2NH_2 \longrightarrow (\text{i-}C_3H_7)_2N-NHCSNHNHCSNH-N(\text{i-}C_3H_7)_2$$

Even with an excess of hydrazine only the same product was obtained, demonstrating the increased reactivity of *N*-isothiocyanatoamines relative to isothiocyanates. The reaction between the latter and hydrazines stops after the introduction of one thiocarbamoyl group,[6] whilst reaction with a second molecule of isothiocyanate proceeds much slower and generally requires heating. By contrast, the above reaction goes to completion in less than one minute. It is noteworthy that methylhydrazine reacts according to the same scheme to 4,4′-bithiosemicarbazides, a class of compound not previously investigated. The reaction between (I) and phenylhydrazine only gives 1,1-diisopropyl-5-phenylthiocarbohydrazide.

$$(\text{i-}C_3H_7)_2N-N=C=S + C_6H_5NHNH_2 \longrightarrow (\text{i-}C_3H_7)_2N-NHCSNHNH-C_6H_5$$

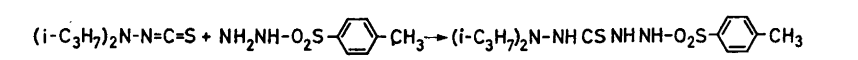
The observation that *N*-methylaniline does not react readily with (I) suggests that the resistance to further reaction is due mainly to steric effects. Of course, the decreased basicity of the thiohydrazide when a phenyl group, rather than an alkyl group, is attached to it, might be a contributory cause. Consistent with this view cyclohexylhydrazine reacts with (I) to give the sterically least hindered 5-cyclohexyl-1,1-diisopropylthiocarbohydrazide whilst the 4-isomer would have been predicted on basicity arguments.

The formation of 5-benzoyl-1,1-diisopropylthiocarbohydrazide from (I) and benzhydrazide was expected from analogy with a study involving phenyl isothiocyanate.[8]

$$(\text{i-}C_3H_7)_2N-N=C=S + C_6H_5CONHNH_2 \longrightarrow (\text{i-}C_3H_7)_2N-NHCSNHNHCOC_6H_5$$

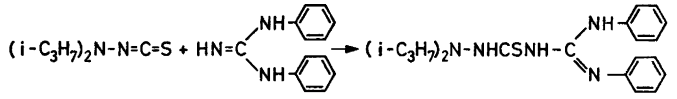
Acylated thiocarbohydrazides have been described previously from ring-opening of 1,3,4-oxadiazol-2-thiones with hydrazines.[9]

Treatment of sulfonylhydrazines with isothiocyanates resulted in substitution at the terminal nitrogen atom with formation of 1-sulfonylthiosemicarbazides.[10] Similarly, in the case of (I), *p*-toluenesulfonohydrazide reacted readily to give 1,1-diisopropyl-5-(*p*-toluenesulfonyl)-thiocarbohydrazide.



4-Amidinothiosemicarbazides are obtainable from the reaction between dithiocarbazic esters and guanidine.[11] As an example of the preparation from

N-isothiocyanatoamines, we have shown that 1,3-diphenylguanidine is transformed into 1,1-diisopropyl-4-(*N*,*N'*-diphenylamidino)-thiosemicarbazide when treated with (I).



(I) reacts with 1,1-dimethylthiosemicarbazide to give a good yield of 1,1-diisopropyl-5-(*N*,*N*-dimethylthiocarbamoyl)-thiocarbohydrazide. Further experiments in this direction have revealed that (I) also reacts with thioamides as more fully discussed in part VI of this series.[12] Results supplementary to the present paper will be presented in part VII.[13]

EXPERIMENTAL

Conditions and equipment used for the physical measurements were those described in part II of this series.[2]

*1-(*N,N-*Diisopropylthiocarbazoyl)-imidazole.* To a solution of imidazole (0.1 mole) in dry chloroform (50 ml) was added a solution of thiophosgene (0.025 mole) in dry benzene (20 ml) at room temperature. The mixture was stirred during the addition and for another ½ h. After filtration of the imidazolium chloride, *N*,*N*-diisopropylhydrazine (0.025 mole) in benzene (10 ml) was added and stirring was continued for ½ h at room temperature. The solution was extracted with three 40 ml portions of water to remove the imidazole dried, and the solvents removed. Recrystallization of the residual yellow crystals (71 % yield) from an ether-pentane mixture afforded colourless crystals, m.p. 129.5—130°C. (Found: C 53.05; H 8.34; N 24.90. Calc. for $C_{10}H_{18}N_4S$: C 53.06; H 8.01; N 24.76). The crude product was satisfactory for the next step in the synthesis.

N-Isothiocyanatodiisopropylamine (I). When the material obtained from the above synthesis was heated in high vacuum in the apparatus previously described for preparation of *N*-isothiocyanatodiethylamine,[1] the monomer (I) was obtained as a yellowish, crystalline product melting at —40°C to —32°C to give a yellow, viscous oil. Experiments using highly purified 1-(*N*,*N*-diisopropylthiocarbazoyl)-imidazole led to diminished yields. The reason for this is probably that the crude starting material begins to melt at *ca.* 100°C, resulting in increased heat transfer and therefore more extensive decomposition of the material not in direct contact with the walls of the glass tube. In this way yield ranging from 50 to 75 % could generally be obtained. Satisfactory elemental analysis of (I) could not be carried out because of the high volatility of the substance. Therefore it was characterized by recording the IR, NMR, and mass spectra discussed in the text. *IR-spectrum* (CCl_4, in cm^{-1}): 2990s, 2940m, 2882m, 2125m sh, 2035vs, 1460m, 1389m, 1372m, 1349w, 1330w, 1190m, 1170m, 1124m, 1108w, 1291w, 1056m, 1000w, 650w, and 602w. *Mass spectrum* (most abundant ions, *m/e*, in parenthesis % relative abundance, with the base peak taken as 100 %): 158 (28), 143 (35), 126 (15), 111 (8), 101 (72), 84 (18), 74 (7), 70 (18), 69 (98), 60 (8), 58 (10), 44 (11), 43 (100), 42 (70), 41 (55), 39 (24), 28 (13), 27 (37).

After standing for several weeks most of the material had crystallized. After washing twice with cold pentane the colourless, crystalline *dimer*, m.p. 96—97°C, was obtained. (Found: C 53.20; H 8.81; N 17.56; S 20.27. Calc. for $C_7H_{14}N_2S$: C 53.12; H 8.92; N 17.71; S 20.26). That dimerization had occurred was shown by the absence of absorptions in the 2000—2200 cm^{-1} range in the infrared spectrum. The structure of this dimer will be discussed in a later paper.[3]

When monomeric I was mixed with a solution of imidazole in a chloroform-tetrachlormethane mixture, heated to the boiling point, and allowed to stand for 1 h at room temperature, recombination took place and *1-(*N,N-*diisopropylthiocarbazoyl)-imidazole* was formed. On evaporation of the solvents a nearly quantitative yield was obtained,

m.p. 123—124°C. A single recrystallization afforded a product identical (m.p., mixed m.p., and infrared spectrum) with the authentic material.

1,1-Diisopropylthiosemicarbazide. An excess of ethereal ammonia was added to (I) at room temperature. The separation of colourless crystals started after 5 min. When allowed to stand a total yield of 10 % was obtained. Evaporation of the ether left an oil which could be recrystallized from water to give an additional 10 % yield of colourless crystals, m.p. 142—143°C. (Found: C 48.10; H 9.84; S 18.21. Calc. for $C_7H_{17}N_3S$: C 47.96; H 9.78; S 18.29).

1,1-Diisopropyl-4-methylthiosemicarbazide. A solution of (I) (60 mg) in ethanol (10 ml) was treated with an excess of ethanolic methylamine solution and left at room temperature for two days. Evaporation of the solvent left a semisolid product which became crystalline on repeated treatment with active carbon in an ethanol-water mixture. A 10 % yield of colourless crystals, m.p. 121—122°C, was recovered. The infrared spectrum of this compound was identical with that of the compound isolated from the reaction of methyl isothiocyanate with *N,N*-diisopropylhydrazine and the melting point of a mixture was not depressed. (Found: C 50.70; H 10.14; N 22.50; S 16.88. Calc. for $C_8H_{19}N_3S$: C 50.75; H 10.12; N 22.20; S 16.93). *IR-spectrum* (KBr, in cm^{-1}): 3319m, 3261m, 3190s, 2974s, 2936m, 2873w, 1551vs, 1513s, 1469m, 1442w, 1421w, 1384m, 1372w, 1361w, 1346w, 1258s, 1179m, 1170m, 1144w, 1127w, 1055m, 1020m, 1011w, 898w, 809w, 752m, 660m br, 560w, 520w, and 490w.

Ethylene-4,4'-bis-(1,1-diisopropylthiosemicarbazide). A solution of (I) and ethylenediamine (a slight excess) in ethanol containing 10 % ether was allowed to stand for two days at —40°C. The colourless, crystalline precipitate was filtered off and washed twice with cold absolute ethanol. The crude product (50 % yield, m.p. 236°C) was submitted to elemental analysis without further purification. (Found: C 50.75; H 9.81; N 22.47; S 16.99. Calc. for $C_{16}H_{36}N_6S_2$: C 51.02; H 9.64; N 22.32; S 17.02). The identity of the product was inferred from the infrared spectrum which was generally similar to that of 1,1-diisopropyl-4-methylthiosemicarbazide described above. *IR-spectrum* (KBr, in cm^{-1}): 3315m, 3193s, 2983m, 2945m, 2880w, 1540vs, 1513s, 1480w, 1465m, 1445w, 1385m, 1376w, 1370w, 1343w, 1325m, 1305m, 1275w sh, 1213s, 1179w, 1164m, 1148m, 1128w, 1095m, 1024w, 1006w, 901w, 822w, 778m, 752w, 635m br, 597w, 561w, 519w, and 493w.

1,1-Diisopropyl-4-phenylthiosemicarbazide. Aniline (50 mg) was added to (I) (87 mg) in absolute ethanol (3 ml), and the reaction mixture kept in an ice-box for 2 h. A crystalline precipitate was obtained by cautious addition of water and scratching with a glass rod. The crystals were filtered off, washed with aqueous ethanol, and dried to give a 75 % yield, m.p. 99—100°C. The colourless crystals were identified by comparison of the infrared spectrum with that of an authentic sample (prepared from phenyl isothiocyanate and *N,N*-diisopropylhydrazine), m.p. 100—101°C (after recrystallization from ethanol), with no depression in the mixed melting point. (Found: C 61.90; H 8.50; N 16.74; S 12.63. Calc. for $C_{13}H_{21}N_3S$: C 62.11; H 8.42; N 16.72; S 12.75). *IR-spectrum* (KBr, in cm^{-1}): 3229m br, 2980m, 2936w, 2877w, 1601m, 1596m, 1550vs, 1501s, 1467m, 1449s, 1388w, 1356m, 1319m, 1305m, 1270s, 1198s, 1179m, 1147m, 1126w, 1109w, 930w, 900w, 789w, 759s, 733m, 692m, 638w br, 615w, 588w, and 501w.

1,1-Diisopropyl-4,4-pentamethylenethiosemicarbazide. Piperidine (40 mg) was added to an equimolar quantity of (I). A moderately exothermic reaction occurred on mixing. The reaction mixture was diluted with methanol (0.75 ml) and heated to a boil for a few seconds. The solution was cooled in an ice-salt bath and water was added dropwise. The colourless oily precipitate was induced to crystallize either by rubbing or by repeated recrystallizations from methanol-water mixtures. The colourless crystals finally obtained were filtered off and washed with ice-cold water. The yield was 42 % with m.p. 61—62°C. (Found: C 59.00; H 10.41; N 17.03. Calc. for $C_{12}H_{25}N_3S$: C 59.21; H 10.35; N 17.26). No expected features were disclosed in the infrared spectrum.

4,4'-Bi(1,1-diisopropylthiosemicarbazide). A slight excess of hydrazine was added dropwise to (I) (60 mg). A vigorous exothermic reaction took place and a transient strong green colour was observed. (This has also been noticed in the reaction of alkyl isothiocyanates with several amines and hydrazines). The reaction mixture crystallized on cooling. Washing with cold ethanol followed by recrystallization from absolute ethanol gave a 85 % yield of colourless crystals, m.p. 240—41°C (dec.). (Found: C 48.28; H 9.24; N 23.81; S 18.37. Calc. for $C_{14}H_{32}N_6S_2$: C 48.24; H 9.25; N 24.11; S 18.40). The absence

of absorptions around 1625 cm^{-1} (NH_2 deformation vibration) in the infrared spectrum excludes that the isomeric 1,1-bis-(*N,N*-diisopropylthiocarbazoyl)-hydrazine had been formed.

*1,2-Bis-(*N,N*-diisopropylthiocarbazoyl)-1-methylhydrazine.* This compound was prepared in the same way from methylhydrazine. However, it proved advantageous to wash with methanol, and recrystallization was performed from benzene or from a benzene-pentane mixture. Yield 28 % of colourless crystals, m.p. *ca.* 180°C (decomp.) dependent on the rate of heating. (Found: C 49.53; H 9.48; N 22.91; S 17.54. Calc. for $C_{15}H_{34}N_6S_2$: C 49.68; H 9.45; N 23.18; S 17.69). The infrared spectrum was essentially the same as that of the foregoing compound except that the two NH absorptions at 3270 cm^{-1} and 770 cm^{-1} were absent.

1,1-Diisopropyl-5-phenylthiocarbohydrazide. Equimolar amounts of (I) and phenylhydrazine were mixed. The reaction mixture crystallized a few seconds after the exothermic reaction had occurred. Washing with ethanol gave a 55 % yield of colourless crystals, m.p. 147—149°C (decomp.) after drying over conc. sulfuric acid. (Found: C 58.40; H 8.42; N 21.20; S 11.87. Calc. for $C_{13}H_{22}N_4S$: C 58.61; H 8.33; N 21.03; S 12.04). In the region around 1600 cm^{-1} in the infrared spectrum only the absorption due to the phenyl ring vibration at 1604 cm^{-1} was observed. Since no absorptions attributable to the NH_2 deformation vibrations are present the possibility that 1,1-diisopropyl-4-phenylthiocarbohydrazide has been formed could be rejected.

1,1-Diisopropyl-5-cyclohexylthiocarbohydrazide. Cyclohexylhydrazine (66 mg) was dissolved in hot ethanol (0.5 ml) and (I) (91 mg) added. The solution was boiled for 1 min, cooled, and the colourless crystalline precipitate, m.p. 126—127°C, was filtered off in good yield. Care must be exercised when washing with ice-cold ethanol since the compound dissolves readily. (Found: C 56.95; H 10.67; N 20.46; S 11.85. Calc. for $C_{13}H_{28}N_4S$: C 57.31; H 10.36; N 20.57; S 11.77). Its identity as the 4-isomer was excluded from a consideration of the region around 1600 cm^{-1} in the infrared spectrum as above.

5-Benzoyl-1,1-diisopropylthiocarbohydrazide. Benzhydrazide (77 mg) and (I) (91 mg) were heated for 1 min in ethanol (0.5 ml). The precipitate formed on cooling was isolated and recrystallized once from ethanol and once from aqueous methanol. If further recrystallization was attempted a deep red colour developed. The colourless crystals were obtained in 58 % yield with m.p. 164—166°C (unsharp). (Found: C 57.05; H 7.56; N 18.80; S 10.83. Calc. for $C_{14}H_{22}N_4OS$: C 57.11; H 7.53; N 19.03; S 10.89). The following absorptions were found in the infrared spectrum in the region from 1500—1700 cm^{-1}: 1687s (C=O), 1603s and 1582w (phenyl), 1546s, and 1515s (thioamide and amide II band). Again, this excludes the isomeric 4-benzoyl derivative.

*1,1-Diisopropyl-5-*p*-toluenesulfonylthiocarbohydrazide.* *p*-Toluenesulfonohydrazide (59 mg) dissolved in boiling absolute ethanol (0.5 ml) was added dropwise to (I) (53 mg). After standing overnight, a 73 % yield of colourless crystals, m.p. 186—187°C, was obtained. (Found: C 48.78; H 7.04; N 16.00; S 18.58. Calc. for $C_{14}H_{24}N_4O_2S_2$: C 48.81; H 7.02; N 16.26; S 18.62). In the infrared spectrum only two absorptions were observed in the 1500—1700 cm^{-1} range: 1600m (phenyl) and 1514s (thioamide band). Accordingly, the 4-isomer has not been formed.

*1,1-Diisopropyl-4-(*N,N'*-diphenylamidino)-thiosemicarbazide,* m.p. 169—170°C, was prepared in the same way from (I) and *N,N'*-diphenylguanidine with benzene as a solvent. (Found: C 65.25; H 7.65; S 8.60. Calc. for $C_{20}H_{27}N_5S$: C 65.00; H 7.37; S 8.68).

*1-(*N,N*-Dimethylthiocarbamoyl)-5,5-diisopropylthiocarbohydrazide.* This was prepared as above in 50 % yield with absolute ethanol as the solvent. The colourless crystals had a m.p. of 176—177°C. (Found: C 43.20; H 8.05; N 25.02; S 23.19. Calc. for $C_{10}H_{23}N_5S_2$: C 43.29; H 8.35; N 25.24; S 23.11). The highest band in the 1500—1700 cm^{-1} region was the thioamide band at 1530 cm^{-1} (vs) which excludes the 2-isomer.

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