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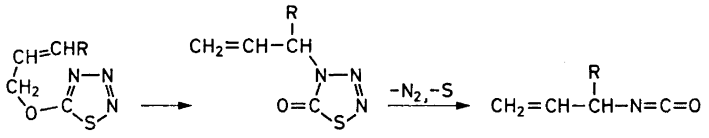
On the Structure of the So-called 4-Substituted 1,2,3,4-Thiatriazoline-5-thiones

CARSTEN CHRISTOPHERSEN and ARNE HOLM

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

The products obtained by treating sodium 1,2,3,4-thiatriazole-5-thiolate with diphenylmethyl-, triphenylmethyl-, and benzoyl chloride have previously been regarded as 4-substituted 1,2,3,4-thiatriazoline-5-thiones. On the basis of both unequivocal synthesis and degradation products, the diphenylmethyl derivative is shown to be 5-(diphenylmethylthio)-1,2,3,4-thiatriazole. Evidence is presented, indicating that the two other derivatives are also 5-substituted 1,2,3,4-thiatriazoles.

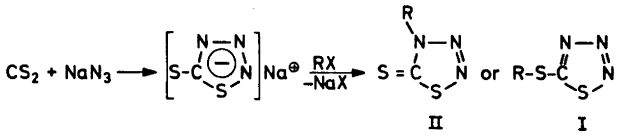
During a study of the allylic rearrangement of 2-alkenyl cyanates, 5-(2-alkenyloxy)-1,2,3,4-thiatriazoles were found to decompose in solution to give sulfur, nitrogen and 2-alkenyl isocyanates, whereas 5-alkoxy-1,2,3,4-thiatriazoles yielded sulfur, nitrogen and alkyl cyanates.[1] From independent experiments, 2-alkenyl cyanates were found to be very labile [1] (no 2-alkenyl cyanates have yet been isolated). They form the corresponding 2-alkenyl isocyanates by a cyclic mechanism. This lability of 2-alkenyl cyanates offers a likely explanation for the results obtained in these decomposition studies. However, as no alkenyl cyanate could be detected, the mechanism which involves rearrangement to a thiatriazoline-5-one prior to decomposition cannot formally be ruled out, although there is no other support for such a step:



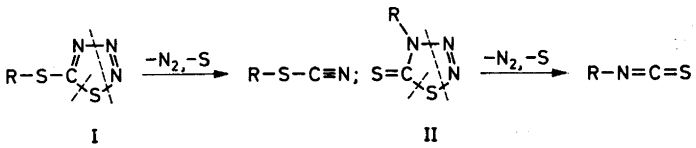
Apparently, no 4-substituted 1,2,3,4-thiatriazoline-5-ones have been reported in the literature, but the preparation of some 4-substituted 1,2,3,4-thiatriazoline-5-thiones (II) have been reported by Lieber *et al.*[2,3] Therefore,

in order to examine thiatriazolines, a closer study of Lieber's compounds was undertaken.

Lieber *et al.* treated sodium 1,2,3,4-thiatriazole-5-thiolate with alkyl and acyl halides, and proposed the products to be either 5-substituted mercapto-1,2,3,4-thiatriazoles (I) or 4-substituted 1,2,3,4-thiatriazoline-5-thiones (II), depending on which organic halide was used:



The structure of the compounds was deduced on the basis of their degradation products and on the basis of IR spectroscopic evidence. It was stated that type I compounds thermally break down to thiocyanates, whereas the isomeric type II compounds generate isothiocyanates, under identical conditions.[2,3]

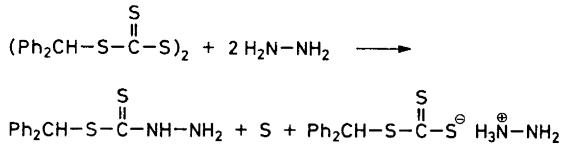


R = a: $(C_6H_5)_3C$; b: $(C_6H_5)_2CH$; c: C_6H_5CO; d: CH_3; e: $C_6H_5CH_2$; f: 4-$(O_2N)C_6H_4CH_2$; g: $C_6H_5COCH_2$; h: 4-$ClC_6H_4COCH_2$; i: 4-$(C_6H_5)C_6H_4COCH_2$; j: CN.

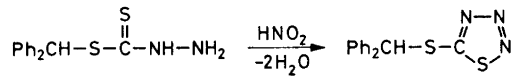
Structure II was proposed for three derivates, a, b, and c, mainly because these compounds were found to yield isothiocyanates, and not thiocyanates, on degradation. However, this structural assignment was questioned by the authors of a review of 1,2,3,4-thiatriazoles[4]. In the absence of conclusive structural data on the compounds, these authors tentatively classify them as Ia, Ib, and Ic, respectively. The aim of this paper is to present evidence that all three compounds, previously assigned structure II, actually are derived from structure I.

Triphenylmethyl thiocyanate and benzoyl thiocyanate are reported to have only a transitory existence, rearranging rapidly to the corresponding isothiocyanates.[5-7] The lack of success in isolating these thiocyanates should, therefore, not be taken as indicative of the existence of the structures IIa and IIc. Although diphenylmethyl thiocyanate can be isolated in a pure state, it is known to be rearranged readily to diphenylmethyl isothiocyanate.[8]

5-(Diphenylmethylthio)-1,2,3,4-thiatriazole. To settle the question of whether the substance designated as IIb by Lieber has the proposed structure, the structure of 5-(diphenylmethylthio)-1,2,3,4-thiatriazole (Ib) was established by unequivocal synthesis. Bis(diphenylmethylthiothiocarbonyl)disulfide, prepared from sodium diphenylmethyl trithiocarbonate, reacted with anhydrous hydrazine, to yield diphenylmethyl dithiocarbazate, sulfur and the hydrazinium salt of diphenylmethyl trithiocarbonic acid.



The dithiocarbazate was treated with nitrous acid to give 5-(diphenylmethylthio-)-1,2,3,4-thiatriazole (Ib). This is a general method for the synthesis of 5-substituted 1,2,3,4-thiatriazoles.[4]



The substance so obtained was shown by melting point, IR and ^{1}H NMR spectra to be identical with the substance designated as IIb by Lieber.

The validity of the structure proof is clearly dependent on the assumption that a rearrangement of 5-(diphenylmethylthio)-1,2,3,4-thiatriazole to 4-diphenylmethyl-1,2,3,4-thiatriazoline-5-thione has not taken place. That no such reaction has occurred was verified by using ^{1}H NMR spectroscopy on the products obtained on degradation of the thiatriazole.

The methine protons of diphenylmethyl isothiocyanate and diphenylmethyl thiocyanate are reported to give signals at 4.10 τ and 4.27 τ, respectively (CCl_4 solutions).[9] In CCl_4, the signal of the methine proton of the so-called IIb appears at 3.80 τ (which is the same chemical shift as that of the methine proton of 5-(diphenylmethylthio)-1,2,3,4-thiatriazole (Ib), synthesized as described above). On standing, the peak at 3.80 τ gradually disappeared, while a peak rose at 4.27 τ, indicating that the sole degradation product was diphenylmethyl thiocyanate. A similar result was found when the authentic thiatriazole (Ib) was allowed to decompose at room temperature.

In contrast to the findings of Lieber *et al.*,[2] we have found that reflux in benzene solution for 2 h gives rise to diphenylmethyl thiocyanate, containing only trace amounts of the isothiocyanate. The reason for the ambiguity may be found in the fact that the degradation products were recrystallized in Lieber's experiment. It is therefore possible that the main product was lost during the purification step.

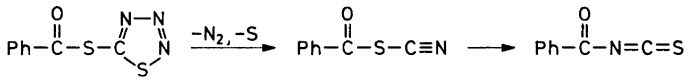
Previously, an IR spectroscopic technique developed by Lieber *et al.* was used, to distinguish between diphenylmethyl thiocyanate and diphenylmethyl isothiocyanate.[10,11] This technique takes advantage of the fact that isothiocyanates give rise to a very strong and broad absorption band at about 2100 cm^{-1}, whereas thiocyanates give a medium intensity, very sharp band around 2160 cm^{-1}. The technique is a very powerful tool in identifying small amounts of isothiocyanates in mixture with thiocyanates. In the case of diphenylmethyl thiocyanate and isothiocyanate, a 1 % content of the isothiocyanate in the thiocyanate could easily be detected. However, a 1 % content of the thiocyanate in isothiocyanate could not be distinguished, since the strong isothiocyanate band has a shoulder (at 2160 cm^{-1}) that may be

mistaken for the thiocyanate absorption. It may thus be concluded that the compound isolated by Lieber *et al.*, in the degradation of the so-called IIb, described as pure diphenylmethyl isothiocyanate, may well have contained small amounts of diphenylmethyl thiocyanate. (The spectra of the two compounds are tabulated in the experimental section.)

The mass spectra of diphenylmethyl thiocyanate and diphenylmethyl isothiocyanate have been recorded, but were almost identical and hardly of diagnostic value.

5-(Benzoylthio)-1,2,3,4-thiatriazole and 5-(triphenylmethylthio)-1,2,3,4-thiatriazole. When the so-called IIc was subjected to thermal degradation in solution, a very sharp band appeared in the IR spectrum at 2170 cm^{-1}. As the decomposition proceeded, a very strong and complex broad band developed around 1981 cm^{-1}. After a sufficient length of time, the band at 2170 cm^{-1} disappeared, and the band around 1981 cm^{-1} became the most intense band in the spectrum. We propose that the 2170 cm^{-1} band is due to the thiocyanate group in benzoyl thiocyanate, and the 1981 cm^{-1} band to benzoyl isothiocyanate (authentic benzoylisothiocyanate [6] in $CHCl_3$ solution exhibits absorption around 1983 cm^{-1}).

These results indicate that it may be possible to isolate the hitherto unknown



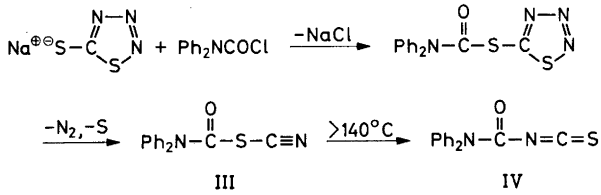
acyl thiocyanates. This is at present being investigated in this laboratory.* It should be noted that we have not been able to detect any triphenylmethyl thiocyanate formed possibly as an intermediate in the decomposition products of the so-called IIa.

On the basis of both the reasons given above and IR spectroscopic evidence, we conclude that the so-called IIc is, in fact, 5-(benzoylthio)-1,2,3,4-thiatriazole. By analogy with this assignment, we propose that the so-called IIa is 5-(triphenylmethylthio)-1,2,3,4-thiatriazole.

5-(N,N-Diphenylcarbamoylthio)-1,2,3,4-thiatriazole. Since *N,N*-diphenylcarbamoyl thiocyanate, in contrast to benzoyl thiocyanate, is a stable compound,[12] *N,N*-diphenylcarbamoyl chloride was considered to be a feasible model substance for acylation of sodium 1,2,3,4-thiatriazole-5-thiolate. Following the general procedure developed by Lieber *et al.*,[2] it was acylated with *N,N*-diphenylcarbamoyl chloride. A compound was obtained which was thermolysed to generate nitrogen, sulfur and *N,N*-diphenylcarbamoyl thiocyanate (identical with an authentic sample [12]). The isomeric isothiocyanate was not a constituent of the thermolysis mixture.

As mentioned above, thiocyanate III is stable and isomerize to the isothiocyanate IV only in the melt.[12,13] The reverse reaction (IV → III) has never been observed. These results strongly suggest that the reaction product from

* Preliminary results have been published in *Acta Chem. Scand.* **25** (1971) 1160 and 1162.



III IV

N,*N*-diphenylcarbamoyl chloride and sodium 1,2,3,4-thiatriazole-5-thiolate is 5-(*N*,*N*-diphenylcarbamoylthio)-1,2,3,4-thiatriazole.

Infrared spectra. There is, according to the afore-mentioned experiments, no reason to believe that any of the derivatives a, b, and c should possess structure II. Instead, structure I is also assigned to these compounds. The frequency assignments of their infrared bands are, therefore, in need of revision. The following vibrations were reported to be characteristic of the two heterocyclic systems.[14]

	Ring-skeletal	Ring-breathing	CH out-of-plane deformations
I	1610 – 1560	1300 – 1260, 1238 – 1222 1105 – 1080, 1125 – 1004	923 – 880
II	1610 – 1560	1320 – 1297, 1226 – 1215 1100 – 1080, 1030 – 1000	912 – 900

Most of the bands in these regions are rather weak and have only little diagnostic value.[15] We have found that the IR spectrum of 5-(methylthio)-1,2,3,4-thiatriazole is devoid of bands in the 1610 – 1560 cm^{-1} region. Thus there is reason to doubt at least the ring-skeletal assignments proposed in the table.

The infrared absorptions of 5-(benzoylthio)-1,2,3,4-thiatriazole in chloroform were reported in more detail.[3,16] A band at 1680 cm^{-1} was assigned to $=N-CO-$; according to the revised structure Ic, this is more probably $-S-CO-$. A doublet at 1590 cm^{-1} was assigned to $-N=N-$ and $-C=C-C_6H_5$, but neither of the structures Ic or IIc contains the latter structural element, however. The revised structure contains neither $=N-C=S$ nor $C=S$, which are reported to absorb at 1450 and 1333 cm^{-1}, respectively. A very broad doublet, with strong absorption, was reported at 1180 cm^{-1}. However, at this position, we find only a single band (at 1179 cm^{-1}), but the very broad and strong band of the solvent (chloroform) appears nearby.

EXPERIMENTAL

Melting points were determined in open tubes and are not corrected. The infrared spectra were recorded, using a Perkin-Elmer model 157 Infracord for routine spectra, and a Perkin-Elmer model 337 Grating Infrared Spectrophotometer for the tabulated spectra (± 5 cm^{-1} over 2000 cm^{-1} and ± 2 cm^{-1} below 2000 cm^{-1}). Abbreviations used: br = broad, sh = shoulder, vs = very strong, s = strong, m = medium, w = weak, vw = very weak. The ^1H NMR spectra were obtained with a Varian A-60 A instrument (60 Mc/s,

and with TMS as internal standard). A double focusing mass spectrometer, type AEI-MS 902, operating at 70 eV, was used to obtain the mass spectra. The samples were introduced through the direct insertion probe.

Sodium diphenylmethyl trithiocarbonate. A solution of diphenylmethanethiol (0.1 mol) in ether (200 ml) was added dropwise, with stirring, to a suspension of sodium hydride (0.1 mol, 55 – 60 % in oil) in ether (250 ml). The reaction mixture was stirred for an additional hour. Carbon disulfide (0.1 mol), dissolved in ether (100 ml), was then added dropwise over a period of 30 min. After stirring for a total of 1 h, petroleum ether (500 ml) was added, and the product isolated by filtration. Yield 29.0 g (97 %), light yellow crystals.

Bis(diphenylmethylthiothiocarbonyl)disulfide. A solution of iodine (0.02 mol) in aqueous potassium iodide (100 ml) was added dropwise to an ice-cold solution of sodium diphenylmethyltrithiocarbonate (0.04 mol) in water (200 ml), until the brown colour of excess iodine was discernible. The reaction mixture was immediately extracted with chloroform (200 ml); the chloroform solution was washed with a 5 % aqueous sodium thiosulfate solution (200 ml), and then with water (100 ml). The dried extract left an oil on evaporation (8.55 g). After 10 h at room temperature, crystals had separated, which were washed with a 1:1 mixture of ether:pentane (50 ml). Yield 3.55 g (37 % based on the iodine added). Recrystallization from a 1:1 mixture of cyclohexane:abs. ethanol left light-yellow crystals of m.p. 137 – 137.5°C. (Found: C 61.35; H 4.17; S 34.60. Calc. for $C_{28}H_{22}S_6$: C 61.09; H 4.03; S 34.88.)

(Diphenylmethylthiothiocarbonyl)hydrazine. Over a period of 15 min, a solution of anhydrous hydrazine (0.02 mol) in chloroform (25 ml) was added dropwise, with stirring to an ice cold solution of bis(diphenylmethylthiothiocarbonyl)disulfide (0.01 mol) in chloroform (50 ml). Stirring was continued for half an hour at room temperature, and the reaction mixture was then filtered. The filtrate was left at room temperature an hour prior to evaporation *in vacuo*. The residue from the evaporation was taken up in benzene (35 ml) and, after filtration, hexane (20 ml) was added to precipitate the product. Yield 2.1 g (77 %). Recrystallization from a 1:1 mixture of ether:pentane left the pure substance, m.p. 139 – 139.5°C. (Found: C 61.40; H 5.10; N 10.03; S 23.56. Calc. for $C_{14}H_{14}N_2S_2$: C 61.31; H 5.15; N 10.21; S 23.33.)

5-(Diphenylmethylthio)-1,2,3,4-thiatriazole. a) (Diphenylmethylthiothiocarbonyl)-hydrazine (2.65 mmol) was dissolved in dioxan (10 ml) and 1.000 N hydrochloric acid (3.00 mmol). Aqueous sodium nitrite (2.65 mmol in 2 ml water) was added dropwise, until the starch-iodide test for nitrous acid was positive. On dilution with water (30 ml), an oily product separated. This was taken up in ether (10 ml), the solution dried over magnesium sulfate, and evaporated *in vacuo*. Yield 0.724 g (96 %). Two recrystallizations from ether gave a substance with m.p. 60.5 – 62.5°C (decomp.). (Found: C 59.00; H 3.99; N 14.68; S 22.58. Calc. for $C_{14}H_{11}N_3S_3$: C 58.94; H 3.89; N 14.73; S 22.44.) The ^{1}H NMR and IR spectra were identical with those described under b). b) Following the directions given by Lieber *et al.*,[2] the so-called 4-diphenylmethyl-1,2,3,4-thiatriazoline-5-thione was prepared. M.p. 60.5 – 62.5°C (decomp.). (Lieber *et al.* 62 – 64°C (decomp.)[2].) ^{1}H NMR spectrum (CCl_4) with signals at 3.80 τ (singlet CH) and from 2.85 to 2.35 τ (complex C_6H_5). IR spectrum (CCl_4, 10 %) 3100w, 3085m, 3062m, 3027m, 1967vw, 1950vw, 1902vw, 1883vw, 1805vw, 1760vw, 1602m, 1587w, 1498s, 1452s, 1380vw, 1327s, 1288wbr. 1244s, 1229s, 1192wbr, 1129wbr, 1094s, 1082s, 1034m, 1004m, 906m, 857vw, 845vw, 836vw, 716s, 699vs, 677sh, 646sh, 632m, 619m, 591sh, 587m, 547vw, 507m, 424wbr cm^{-1}.

Degradation of 5-(diphenylmethylthio)-1,2,3,4-thiatriazole. a) The thiatriazole, prepared *via* the hydrazine, was dissolved in carbon tetrachloride (32 mg in 0.5 ml CCl_4) in an NMR tube. After 72 h at room temperature, 50 % had been transformed to diphenylmethyl thiocyanate as evidenced by the signals at 3.80 and 4.27 τ. After 140 h at room temperature, followed by 2 h at 65°C, only the signal at 4.27 τ was left, signifying that, within the accuracy of the measurement, only thiocyanate was formed. b) The thiatriazole (1.0 g), prepared according to Lieber *et al.*,[2] was dissolved in carbon tetrachloride (10 ml). After 40 h at room temperature, 35 % thiocyanate had been formed. After 46 h at room temperature, followed by 30 min at reflux temperature, only the peak at 5.73 τ was left. Sublimation at 70°C and 0.1 mmHg gave a mixture corresponding to 88 % diphenylmethyl isothiocyanate and 12 % diphenylmethyl thiocyanate. c) To reinvestigate the degradation experiment of Lieber *et al.*, the thiatriazole (1.0 g) in benzene (5 ml) solution was heated under reflux for 2 h, as described. Evaporation of the solvent left

a mixture consisting mainly of the thiocyanate and sulfur. ^{1}H NMR spectroscopy revealed an isothiocyanate content of about 1 – 2 %. In accordance with this, the IR spectrum ($CHCl_3$, 10 %) exhibited, apart from the bands of the thiocyanate, two very weak bands at *ca.* 2075 cm^{-1} and 601 cm^{-1}, respectively.

Diphenylmethyl thiocyanate was prepared as described in the literature.[6] ^{1}H NMR spectrum (CCl_4) with signals at 7.32 τ (singlet C_6H_5) and 5.73 τ (singlet CH). IR spectrum (CCl_4, 10 %), 3115w, 3100m, 3075m, 3040m, 3015sh, 2160s, 1965vw, 1948w, 1892vw, 1872vw, 1798w, 1750vw, 1590w, 1575w, 1495s, 1450s, 1372vw, 1325w, 1315vw, 1203sh, 1185mbr, 1157vw, 1105vw, 1088m, 1031m, 1002w, 914vw, 855vw, 697vs, 686sh, 628m, 616m, 589m, 495w, 470w cm^{-1}.

Diphenylmethyl isothiocyanate was prepared as described in the literature.[6] ^{1}H NMR spectrum (CCl_4) with signals at 7.30 τ (singlet C_6H_5) and 5.90 τ (singlet CH). IR spectrum (CCl_4, 10 %), 3108sh, 3090m, 3068m, 3030s, 3008sh, 2888w, 2160sh, 2136sh, *ca.* 2060vsbr, 1943m, 1893vw, 1875w, 1800w, 1753vw, 1593m, 1583w, 1491s, 1453vs, 1378w, 1341s, 1325m, 1294m, 1278s, 1247w, 1182w, 1155vw, 1107vw, 1072w, 1030s, 1002w, 915vw, 857m, 718s, 699vs, 675w, 635s, 619m, 602s, 530wbr, 465wbr cm^{-1}.

5-(Benzoylthio)-1,2,3,4-thiatriazole. Prepared according to the directions given by Lieber *et al.* for 4-benzoylthiatriazoline-5-thione.[2] M.p. 93 – 94°C (decomp.) (lit. 92 – 93°C (decomp.), 92 – 94°C (decomp.))[2] The ^{1}H NMR spectrum ($CDCl_3$) exhibits signals from 2.56 to 1.74 τ (complex, C_6H_5). IR spectrum ($CHCl_3$, saturated), 3063w, 3006w, 1803vw, 1743vw, 1687vs, 1595m, 1583m, 1515vw, 1488vw, 1451s, 1338m, 1316w, 1303vw, 1178s, 1160w, 1097s, 1068vw, 997m, 945vw, 925sh, 897vs, 854sh, 703w, 683vs, 667m, 652m, 642s, 613w cm^{-1}.

Degradation of 5-(benzoylthio)-1,2,3,4-thiatriazole. A saturated solution of the thiatriazole in chloroform was kept at 46°C. After 15 min, the IR spectrum showed weak absorptions at 2170 cm^{-1} and at 1760 cm^{-1}. As these bands (which are thought to be due to the thiocyanate and carbonyl groups in benzoyl thiocyanate) increase in intensity, the bands of benzoyl isothiocyanate slowly appear in the spectrum. After 5 h at 46°C, the bands of benzoyl isothiocyanate at 1981, 1936 (NCS), and at 1691 cm^{-1} (C=O) are among the most intense bands in the spectrum, while the 2170 and 1760 cm^{-1} bands are still strong. When the solution was left for further 18 h at room temperature, the IR spectrum became identical with that of authentic benzoyl isothiocyanate.

5-(Triphenylmethylthio)-1,2,3,4-thiatriazole. Prepared according to the directions given by Lieber *et al.* for 4-triphenylmethylthiatriazoline-5-thione.[2] M.p. 99 – 100° (decomp.) (lit. 91 – 92°C (decomp.), 102 – 104° (decomp.)).[2] IR spectrum ($CHCl_3$, 10 %), 3088m, 3061m, 3034m, 3006m, 1973vw, 1953w, 1903vw, 1810vw, 1773vw, 1593w, 1578w, 1493s, 1445s, 1385vw, 1319m, 1306m, 1185m, 1158vw, 1142w, 1086sh, 1082sbr, 1035m, 1009sh, 1002m, 912vw, 889vw, 836mbr, 698vs, 665w, 649vw, 630s, 626s, 617m, 545vw, 519w, 502m, 439wv cm^{-1}.

5-(Methylthio)-1,2,3,4-thiatriazole.[2] IR spectrum (CCl_4, 10 %), 2937m, 1412s, 1407m, 1599sh, 1334s, 1312s, 1284m, 1243vs, 1227s, 1117m, 1095vs, 1061sh, 1000s, 973m, 965sh, 905s, 873vw, 856vw, 844vw, 835vw, 707m, 697m, 642w, 607w, 546w cm^{-1}.

5-(N,N-Diphenylcarbamoylthio)-1,2,3,4-thiatriazole. A solution of the sodium salt of 1,2,3,4-thiatriazole-5-thiole (0.036 mol), prepared according to Lieber *et al.*,[2] in 10 ml of water, was added dropwise to a solution of *N,N*-diphenylcarbamoyl chloride (0.036 mol) in acetone (40 ml). The reaction mixture was left for 5 h at room temperature. Cooling in solid CO_2-acetone, followed by filtration, left a solid, which was thoroughly washed with 75 ml of ether. The residue was taken up in 25 ml of chloroform and dried over anhydrous magnesium sulfate. The dry chloroform solution was mixed with an equal amount of dry ether, and cooled in solid CO_2-acetone. Filtration yielded a solid, which was dried *in vacuo* over conc. sulfuric acid at room temperature for a few minutes, and then kept in a refrigerator at −30°C.

Degradation of 5-(N,N-diphenylcarbamoylthio)-1,2,3,4-thiatriazole. The thiatriazole (5.34 mmol) in dry benzene (10 ml) was left for 90 hours at room temperature. After removal of the precipitated sulfur, a solid was left on evaporation of the benzene. The IR spectrum of the product was superimposable upon that of an authentic sample of *N,N*-diphenylcarbamoyl thiocyanate.[12] The yield was almost quantitative.

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