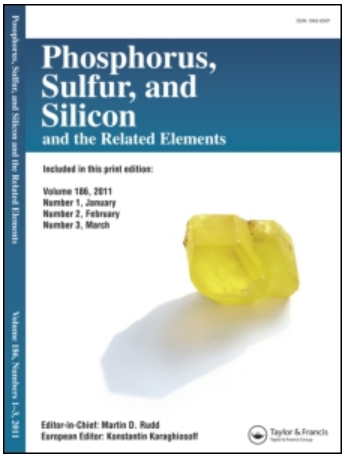

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THIOCARBONYL TRANSFER REAGENT CHEMISTRY. IV. THE PREPARATION OF 1,1- AND 1,2-DISUBSTITUTED THIOSEMICARBAZIDES UNSUBSTITUTED IN THE 4-POSITION

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THIOCARBONYL TRANSFER REAGENT CHEMISTRY. IV. THE PREPARATION OF 1,1- AND 1,2-DISUBSTITUTED THIOSEMICARBAZIDES UNSUBSTITUTED IN THE 4-POSITION[1]

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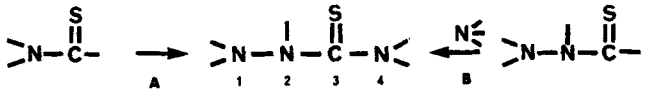
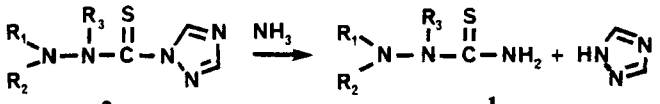
The utility of 1,1'-thiocarbonyldi(1,2,4-triazole) **3** as a thiocarbonyl transfer reagent capable of sequential substitution by amines and hydrazines is demonstrated.

Thiosemicarbazides (**1**) have been known for many years and are useful starting materials for the synthesis of a wide variety of heterocycles.[2] The two major approaches in the synthesis of thiosemicarbazides are transfer of either a thiocarbamoyl (>N—C(=S)—) group to a hydrazine or a thiocarbazoyl (>N—N(—)—C(=S)—) unit to an amine.[3] Various reagents are available (isothiocyanates and thiocarbamoyl halides for accomplishing thiocarbamoyl transfer (Scheme 1, path A). For thiocarbazoyl transfer (Scheme 1, path B), the selection is more restrictive.[4] In sum, thiosemicarbazides disubstituted in the 4-position can usually be obtained.



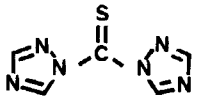
SCHEME 1

The techniques available for the more synthetically useful thiosemicarbazides *un*substituted in the 4-position are quite limited. By either routes A or B (Scheme 1) literature methods are inadequate.[5] One possible route briefly mentioned involves the synthesis of 1,2-diphenylthiosemicarbazide **1e**.[6] The route was believed to involve the intermediate formation of **2e** from thiophosgene and 1,2,4-triazole. A careful reinvestigation of this reaction using 1,1'-thiocarbonyl (1,2,4-triazole) **3** gave a yellow crystalline compound (97% yield, mp 90–91°C) with the characteristic properties



2 1

expected from **2e**. On treatment with conc. ethanolic ammonia, **1e** was obtained in 86% yield.

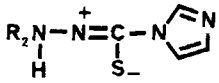


3

Reactions with **3** and other 1,1- or 1,2-disubstituted hydrazines result in thiocarbazoyltriazoles **2**. Upon treatment with ammonia these are easily transformed into thiosemicarbazides in good yield (Table I) demonstrating the general usefulness of the procedure.

1,1,2-Trimethylthiosemicarbazide (**1i**) could also be prepared in 88% yield from trimethylthiocarbazoyltriazole and ammonia. In this case, however, the thiocarbazoylation proceeds at a much slower rate and it was necessary to heat the reactants in a sealed glass vessel to 60°C for 40 h.[8]

The structure of the thiocarbazoyltriazoles was further investigated since it has been shown that 1,1-dialkylthiocarbazoylimidazoles[9] possess the zwitterionic structure **4**. We found that the triazole analogs **2a** and **1g** had similar structures, while **2b**



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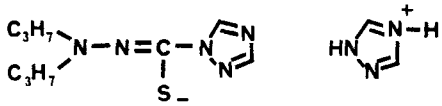
could be isolated only as triazole salt **5**.



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From the reaction of **3** with 1,1-dimethylhydrazine a crystalline compound was isolated having an elemental analysis between that of a structure corresponding to a triazole salt and that of **4**. The ^{1}H NMR spectrum was in accordance with a formula having two amphoionic molecules and one triazole molecule; the infrared spectrum confirmed the existence of strong hydrogen bonds. We therefore propose arrangement **6** to account for these properties. On heating **6** to 80°C in vacuum the hydrogen bonded triazole is eliminated and **2j** is obtained having a structure similar to **2a** and **2g**.

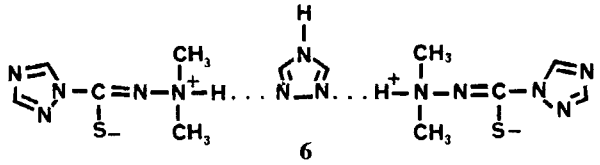

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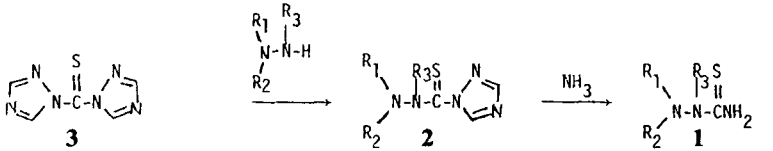
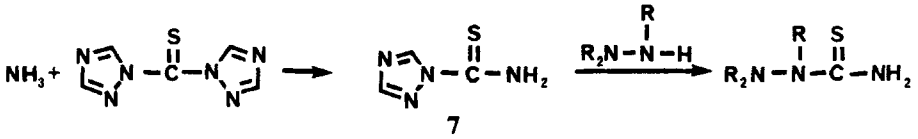
TABLE I



Number	R_1, R_2, R_3	Yield %	mp °C	Number	Yield %	mp °C
2a	i-C_3H_7—, i-C_3H_7—, H—[a]	70	152–153	**1a**	40	139–140[d]
2b	n-C_3H_7—, n-C_3H_7—, H—[b]	50	80–81	**1b**	86	121–122
2c	C_6H_5—, H—, i-C_3H_7—	77	94–95	**1c**	98	193–194
2d	C_6H_5—, C_6H_5—, H—	78	121–122	**1d**	58	202–203[3]
2e	C_6H_5—, H—, C_6H_5—	97	90–91	**1e**	98	183–184[h]
2f	C_6H_5—, H—, C_2H_5	—	oil[c]	**1f**	64	147–148
2g	—$(CH_2)_5$—, H—[a]	66	136–137	**1g**	75	168–169
2h	$C_6H_5CH_2$—, $C_6H_5CH_2$—, H—	94	138–139	**1h**	74	144–145
2i	CH_3—, CH_3—, CH_3—	47	58–60	**1i**	88	89–91[f]
2j	CH_3, CH_3—, H—	90	115–116	**1j**	74	184–185[g]

[a]Amphoionic structure.
[b]Isolated as a triazolium salt.
[c]The crude product was used for the preparation of **1f**.
[d]Lit. mp 142–143, Ref. 4.
[e]Lit. mp 202, Ref. 12.
[f]Described as a hydrochloride, Ref. 3.
[g]Lit. mp 184–185, Ref. 3.
[h]Lit. mp 182–183, Ref. 3.



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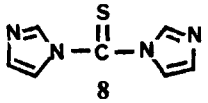
SCHEME 2

Thiocarbonylditriazole (**3**) could be used to obtain 4-unsubstituted thiosemicarbazides via Route A. The reaction involves initial treatment with ammonia to give *N*-thiocarbamoyltriazole **7** followed by reaction with hydrazines (Scheme 2). The same reaction carried out with thiocarbonylimidazole, **8** resulted in a compound



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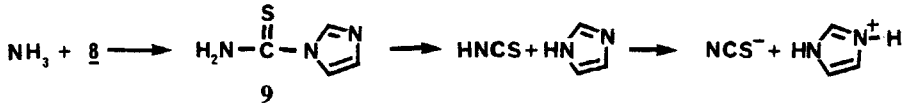
with an elemental analysis corresponding to thiocarbamoylimidazole **9**. The compound, however, was shown to be imidazolium thiocyanate **10**.[10] The reaction may be envisioned to proceed via dissociation of the initial product **9** into thiocyanic acid and imidazole,[11] followed by protonation of the imidazole (Scheme 3). Further experiments with **7** failed to produce the desired thiosemicarbazides.



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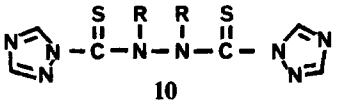
SCHEME 3

In summary, *N*-thiocarbazoyltriazoles **2** provide a valuable and general route to 1,1-disubstituted-4-unsubstituted thiosemicarbazides **1** in good overall yield. Also, 1,3-diaryl- and 1-aryl-2-alkyl-thiosemicarbazides can be prepared by this method. The reason why 1-alkyl-2-arylthiosemicarbazides cannot be made using **3** can be ascribed to the fact that the most basic nitrogen atom (alkyl substituted) attacks the thiocarbonyl carbon.

1,2-Dialkyl compounds are not accessible by this method since the reaction between **3** and 1,2-dialkylhydrazines results in the formation of compounds with structures corresponding to **10**. Similarly, the reaction between monoalkylhydrazines and **3** gives products, the formation of which can be explained by an intermediate analogous to **10**.



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Finally, it should be mentioned that thiocarbazoyltriazoles **2** not only react with ammonia, but also with amines and hydrazines (Table II). In the latter case thiocarbonohydrazides **11a–e** are obtained.

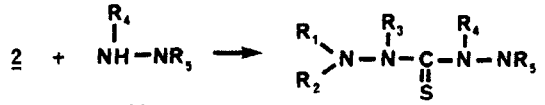

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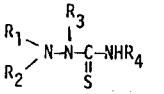
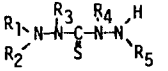
TABLE II

Thiosemicarbazides, 

R_1, R_2, R_3, R_4	Method	No.	Analysis (C, H, N: Calcd./Found)	Mp °C	Yield %
CH_3—, CH_3—, CH_3—, $C_6H_5CH_2$—	A	**1k**	59.15, 7.67, 18.82/59.31, 7.73, 18.82	52–54	59
CH_3—, CH_3—, H, C_6H_{11}—	B	**1l**	53.69, 9.51, 20.88/53.80, 9.61, 20.95	149–150[a]	65
—$(CH_2)_5$—, H, $C_6H_5CH_2$—	B	**1m**	62.61, 7.68, 16.85/62.60, 7.67, 17.09	187–188	96
i-C_3H_7—, *i*-C_3H_7—, H, C_6H_{11}—	B	**1n**	60.65, 10.57, 16.23/60.37, 10.80, 16.48	100–101	58
C_3H_7—, C_3H_7, H, C_6H_{11}—	B	**1o**	60.65, 10.57, 16.33/60.75, 10.37, 16.27	53–54	90
C_6H_5—, H—, *i*-C_3H_7—, $C_6H_5CH_2$—	B	**1p**	68.19, 7.07, 14.04/68.00, 7.20, 14.22	118–119	87
C_6H_5—, H—, C_6H_5—, C_6H_{11}—	C	**1q**	70.11, 7.12, 12.91/70.25, 7.17, 12.98	177–178	86
Thiocarbonohydrazides 					
i-C_3H_7—, *i*-C_3H_7—, H, H—, H—	B	**11a**	44.17, 9.53, 29.45/44.29, 9.55, 29.44	133–135	68
C_3H_7—, C_3H_7—, H—, H—, H—	B	**11b**	44.17, 9.53, 29.45/44.44, 9.62, 29.15	101–102	79
C_6H_5—, H—, C_6H_5—, H—, H—, H—	C	**11c**	60.44, 5.46, 21.69/60.35, 5.64, 21.59	125–126	87
C_6H_5—, H—, C_6H_5—, CH_23, H—	C	**11c**	61.73, 5.92, 20.58/61.65, 5.81, 20.48	112–113	75
C_6H_5—, H—, C_6H_5—, H—, C_6H_5—	D	**11d**	68.23, 5.42, 16.76/68.15, 5.34, 16.82	131–132	96

[a]Lit.[3] mp 150–151°.

EXPERIMENTAL

Conditions and equipment used for the physical measurements were those described previously.[1]

Preparation of **2a**. To a well-stirred solution of **3** (1.8 g, 0.01 mol) in $CHCl_3$ (10 ml) maintained at room temperature was added, dropwise, over a period of 20 min, a solution of 1,1-diisopropylhydrazine (1.16 g, 0.01 mol) in CCl_4 (20 ml). After addition was completed the colorless crystals were filtered (1.75 g) and the filtrate taken to dryness. The residue consisted of 1.1 g of greasy yellowish crystals. Both fractions were recrystallized from ethanol giving a total yield of 1.6 g of **2a** (70%) with a mp of 152–153°C. Calcd. for $C_9H_{17}N_5S$: 47.55, 7.54, 30.81; Found: 47.37, 7.46, 30.83.

Preparation of **2b**. A solution of **3** (1.8 g, 0.01 mol) in $CHCl_3$ (15 ml) was slowly added to a solution of *N,N*-dipropylhydrazine (1.16 g, 0.01 mol) in CCl_4 (25 ml). The colorless crystals formed were filtered (0.6 g) and shown to be triazole. The filtrate was taken to dryness *in vacuo*. The residue was a pale yellow oil which slowly crystallized on standing. After 24 h the crude product was recrystallized from a benzene/pentane mixture to give the triazole salt of **2b** (1.05 g) with a mp of 80–81°C. By adding more pentane to the filtrate another 0.225 g was obtained, giving a total yield of 50%. Calcd. for $C_{11}H_{20}N_8S$: 44.57, 6.80, 37.81; Found: 44.66, 7.06, 37.40.

Preparation of **2c**. A mixture of **3** (1.8 g, 0.01 mol) and *N*-isopropyl-*N'*-phenylhydrazine (1.5 g, 0.01 mol) in acetone (20 ml) was refluxed for 45 min after which the solvent was removed *in vacuo*. The residue was dissolved in a hot ethanol/water mixture which on cooling gave 2.0 g yellow crystals (77%) with a mp of 94–95°C. Calcd. for $C_{12}H_{15}N_5S$: 55.14, 5.79, 26.80; Found: 55.00, 5.74, 26.63.

Preparation of **2d**. To a solution of *N,N*-diphenylhydrazine hydrochloride (2.20 g, 0.01 mol) in dry ether (50 ml) was added a solution of triethylamine (1.24 g, 0.01 mol) in dry ether (50 ml). The mixture was shaken for 2 h, after which triethylammonium chloride was removed by filtration. A solution of **3** (1.80 g, 0.01 mol) in CH_2Cl_2 (25 ml) was added to the filtrate and the mixture was refluxed for 20 min. After standing for 2 h at room temperature, the solvents were removed *in vacuo*. The residue (a violet colored oil) was dissolved in boiling ethanol. On cooling, slightly violet colored crystals were formed (2.3 g, 78%). Recrystallization from pentane gave yellowish crystals with a mp of 121–122°C in accordance with that previously reported.[4]

Preparation of **2e**. A mixture of **3** (1.80 g, 0.01 mol) and 1,1-diphenylhydrazine (1.84 g, 0.01 mol) in acetone (15 ml) was refluxed for 1.5 h. After cooling the mixture to 0°C water was added and the resultant viscous oil was worked with a glass rod to afford yellow crystals (2.90 g, 97% yield). Recrystallization from ethanol gave yellow crystals with a mp of 90–91°C. Calcd. for $C_{15}H_{13}N_5S$: 60.99, 4.44, 23.72; Found: 61.10, 4.65, 23.46.

Preparation of **2f**. The same procedure as for **1e** was used. It was, however, not possible to induce crystallization to the red-brown oil obtained, thus the crude product was used directly for the preparation of **2f**.

Preparation of **2g**. To a stirred solution of *N*-aminopiperidine (2.00 g, 0.02 mol) in CCl_4 (30 ml) **3** (3.60 g, 0.02 mol) in $CHCl_3$ (20 ml) was dropwise added over a period of 30 min. Stirring was continued for another 30 min after which 1.4 g triazole was collected. The filtrate was evaporated to dryness *in vacuo*. The crystalline residue was recrystallized from ethanol yielding 2.60 g colorless crystals with a mp of 136–137°C. From the filtrate another 0.20 g was obtained giving a total yield of 66%. Calcd. for $C_8H_{13}N_5S$: 45.47, 6.20, 33.15; Found: 45.63, 6.29, 33.10.

Preparation of **2h**. To a stirred solution of **3** (1.80 g, 0.01 mol) in CH_2Cl_2 (15 ml) was added a solution of 1,1-dibenzylhydrazine (2.12 g, 0.01 mol) in $CHCl_3$ (15 ml). During the addition crystals began to separate. The mixture was stirred overnight. Triazole (0.480 g) was collected and the filtrate evaporated to dryness. The residue consisted of pale yellow crystals which were crystallized from acetone to give colorless crystals (3.05 g, 94%, mp 138–139°C). Calcd. for $C_{17}H_{17}N_5S$: 63.13, 5.30, 21.66; Found: 63.32, 5.27, 21.48.

Preparation of **2i**. A solution of **3** (6.48 g, 0.036 mol) in CH_2Cl_2 (85 ml) was added over 1 h to a solution of trimethylhydrazine (2.66 g, 0.036 mol) in CH_2Cl_2 (40 ml). The colorless crystals formed were filtered (1.37 g) and shown to be triazole. The filtrate was evaporated to dryness *in vacuo*. The residue (a pale yellow oil) was eluted through a column of silica gel (100 g) with a methylene chloride–ether (1 : 1) solvent blend. Collection of the appropriate fractions afforded 3.6 g of a yellow oil. The oil was dissolved in an ether–pentane mixture, which on cooling to 0°C gave pale yellow crystals (3.1 g, 47%). A small portion

was recrystallized from ether–pentane to give colorless crystals, mp 58–60°C. Calcd. for $C_6H_{11}N_5S$: 38.89, 5.98, 37.80; Found: 38.82, 6.04, 38.08.

Preparation of **2j**. A solution of *N,N*-dimethylhydrazine (0.60 g, 0.01 mol) in CCl_4 (15 ml) was added to a stirred solution of **3** (1.80 g, 0.01 mol) crystals (2.08 g) were filtered off. An NMR spectrum was consistent with **5**. The crystals were heated to 80°C in a sublimation apparatus for 3 h at a pressure of 12 mmHg. Crystals of pure triazole were collected from the condenser, and the residue was shown to be analytically pure **2j** with a melting point of 115–116°C; yield: 1.53 g (90%). Calcd. for $C_5H_9N_5S$: 35.07, 5.30, 40.91; Found: 34.99, 5.33, 41.06.

Preparation of **1a**. Two ml of conc. ammonia were added to a hot solution of **1a** (0.23 g, 0.001 mol) in ethanol (5 ml). The mixture was heated to the boiling point for a few minutes and left at room temperature for two weeks after which the solvents were removed *in vacuo*. The crystalline residue was recrystallized from water to give 0.050 g (40%) of colorless crystals with a mp of 139–140°C, lit.[4] 142–143°C. Calcd. for $C_7H_{17}N_3S$: C, 47.96; H, 9.78; N, 23.97; Found: C, 47.60; H, 9.43; N, 24.18.

Preparation of **1b**. Two ml of conc. ammonia were added to a solution of **1b** (triazole salt) (0.29 g, 0.001 mol) in warm ethanol (4 ml). The mixture was left for one week at room temperature. Addition of water and cooling to 0°C afforded 0.150 g (86%) of colorless crystals with a melting point of 121–122°C. The crystals were submitted for analysis without any purification. Calcd. for $C_7H_{17}N_3S$: 47.96, 9.78, 23.97; Found: 47.92, 9.60, 24.00.

Preparation of **1c**. Concentrated ammonia (2 ml) was added to a solution of **2c** (0.299 g, 0.001 mol) in warm ethanol (8 ml). The mixture was left overnight at room temperature. Addition of water and cooling to 0°C afforded colorless crystals (0.205 g, 98%) with a mp of 193–194°C. The crystals were submitted for analysis without any purification. Calcd. for $C_{10}H_{15}N_3S$: 57.38, 7.22, 20.08; Found: 57.17, 6.96, 20.10.

Preparation of **1d**. The same procedure was used as for the synthesis of **2c** part from substituting concentrated ammonia with a 10 M ammonia in ethanol. Recrystallization from ethanol-water afforded colorless crystals with mp 202–203°C; lit.[12] 202°C (yield 58%).

Preparation of **1e**. The same procedure was used as for the synthesis of **1c**. Colorless crystals were obtained with a mp of 183–184°C; lit.[3] 182–183°C (yield 98%).

Preparation of **1f**. Concentrated ammonia (2 ml) was added to a solution of the red-brown oil believed to be **2f** (0.250 g, 0.0018 mol) in ethanol (3 ml). After standing for one week, addition of water afforded crystals. Recrystallization from water gave colorless crystals (0.125 g, 64%) with a mp of 147–148°C. Calcd. for $C_9H_{13}N_3S$: 55.35, 6.71, 21.52; Found: 55.30, 6.88, 21.49.

Preparation of **1g**. Concentrated ammonia (2 ml) was added to a solution of **2g** (0.211 g, 0.001 mol) in warm ethanol (4 ml). The mixture was left for 10 days; after addition of water, crystals began to separate. Cooling and filtration gave colorless crystals (0.120 g, 75%) with a mp of 168–169°C. The crystals were submitted for analysis without any purification. Calcd. for $C_6H_{13}N_3S$: 45.25, 8.23, 26.39; Found: 45.42, 8.32, 26.32.

Preparation of **1h**. Ammonia (1 ml of 10 M) in ethanol was added to a solution of **2h** (0.323 g, 0.001 mol) in hot ethanol (5 ml). After the mixture had been heated to boiling it was left for 24 h. Cooling and dropwise addition of water afforded crystals which were recrystallized from ethanol. The colorless crystals had a mp of 72–74°C and contained one mole of ethanol. Calcd. for $C_{17}H_{23}N_3SO$: 64.33, 7.30, 13.24; Found: 64.71, 7.23, 13.41. Recrystallization from benzene–hexane gave crystals which fit an analysis for 2 moles of **1h** and one mol benzene. However, drying the crystals containing ethanol for 6 h over P_2O_5 at 50°C in high vacuum gave crystals with a mp of 144–145°C fitting the analysis of **2h** (yield 0.20 g, 74%). Calcd. for $C_{15}H_{17}N_3S$: 66.38, 6.31, 15.49; Found: 66.00, 6.31, 15.43.

Preparation of **1i**. A solution of **2i** (0.555 g, 0.003 mol) in 10 M ammonia in ethanol (1.5 ml) was heated to 50°C in a sealed glass tube for 44 h, after which the solvent was removed *in vacuo*. The residue was eluted through a slurry packed (methylene chloride) silica gel (25 g) column (elution was 1 : 1 with CH_2Cl_2–ether). Ten-ml fractions were collected and from fractions 9–14 a total of 0.340 g colorless crystals with a mp of 89–91°C was gained. Only the melting point of the hydrochloride of **2i** could be found in the lit.;[3] yield 88%. Calcd. for $C_4H_{11}N_3S$: 36.08, 8.33, 31.56; Found: 36.31, 8.56, 31.20.

Preparation of **1j**. A solution of **6** (0.822 g, 0.002 mol) in concentrated ammonia (2 ml) was heated to 50°C in a sealed glass tube for 48 h. The solution was cooled to 0°C whereupon colorless crystals were

formed. Filtration gave 350 mg (74%) of the target compound (mp 180–182°C, lit.[3] 184–185°C). Recrystallization from water raised the melting point to 182–184°C.

Preparation of **1k–q** *and* **12–16**

Method A. The compounds were dissolved in $CHCl_3$. After 24 h pentane was added and the precipitated triazole filtered. The filtrate was evaporated to dryness, and the pale yellow crystals were recrystallized from ethanol/water.

Method B. The compounds were mixed in ethanol and refluxed for 1 h. After cooling in ice/water, the crystals were filtered. In some cases it was necessary to add water to the solution to cause precipitation. The crystals were washed with cold ethanol (or ethanol/water) and submitted for analysis without further purification.

Method C. The same procedure was used as for method B, with the exception that the mixture was heated to the boiling point for one minute and then cooled.

Method D. The same procedure was used as for method B, with the exception that the mixture was not refluxed but stirred for 24 h.

N-Thiocarbamoyltriazole (**7**). To a solution of **3** (0.45 g, 0.0025 mol) in $CHCl_3$ (2 ml) was added 10 M ammonia in ethanol (0.25 ml). A strongly exothermic reaction took place and colorless crystals began to separate. After cooling the solution the crystals were filtered and submitted for analysis without any purification (yield 0.21 g, 66%, mp 114–115°C). Calcd. for $C_3H_4N_4S$: 28.11, 3.14, 43.73; Found: 28.10, 3.28, 43.89.

2-Methylthiosemicarbazide. A solution of methylhydrazine (0.092, 0.002 mol) in ethanol (1 ml) was added to a solution of **6** (0.256, 0.002 mol) in ethanol (2 ml). Cooling the mixture to 0°C afforded crystals which were recrystallized from water to give 0.125 g (60%) of colorless crystals with a mp of 173–174°C, lit.[3] 173–174°C. The infrared spectrum was identical with that of an authentic sample.

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REFERENCES AND NOTES

1. For part III in this series, see C. Larsen and D. N. Harpp, *J. Org. Chem.*, **46** (1981), 2465.
2. K. A. Jensen, U. Anthoni, B. Kägi, C. Larsen and P. T. Pedersen, *Acta Chem. Scand.*, **22** (1968).
3. U. Anthoni, C. Larsen and P. H. Nielsen, *Acta Chem. Scand.*, **20**, (1966), 1714; *ibid.*, **21** (1967), 1201 and 2061.
4. Ref. 2, p. 17.
5. Ref. 2, pp. 9 and 10.
6. M. Battegay and E. Hégazi, *Helv. Chim. Acta*, **16** (1933), 999.
7. Ref. 2, pp. 11 and 12.
8. Ref. 2, pp. 14 and 39.
9. C. Larsen, K. Steliou and D. N. Harpp, *J. Org. Chem.*, **43** (1978), 337.
10. The decreased reactivity of the fully substituted thiocarbazoyltriazole, compared to the partly substituted compound was not unexpected, knowing the difference in reactivity between mono- and dialkylthiocarbamoyltriazoles, where the diethyl compound does not react at all with amines (see Ref. 9).
11. U. Anthoni, C. Larsen and P. H. Nielsen, *Acta Chem. Scand.*, **23** (1969), 1231.
12. C. Larsen, Unpublished results.
13. H. A. Stabb and G. Walther, *Justus Liebig Ann. Chem.*, **657** (1962), 104.
14. D. Tivoli, *Gaz. Chim. Ital.*, **22** (1892), II, 386.