Polish J. Chem., **75**, 975–982 (2001)

Reactions of Thioesters with Organic Azides – A Novel Access to Imidates and Thioimidates*

by G. Mlostoń[1], J. Romański[1] and H. Heimgartner[2**]**

[1]*Section of Heteroorganic Compounds, University of Łódź, Narutowicza 68, PL-90-136 Łódź, Poland*
[2]*Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland*

(Received February 12th, 2001)

The reaction of O-methyl thiocarboxylates **8a**, **b** with organic azides at 110°C yielded the corresponding imidates of type **9**, which were easily hydrolyzed to give amides **10**. The formation of **9** can be rationalized by a 1,3-dipolar cycloaddition of the azide with the C=S group, followed by the "twofold extrusion" of N_2 and S. The analogous reaction with methyl dithiobenzoate (**11**) led to thioimidates **13**. On heating, the latter were transformed into thioamides **12**.

Key words: 1,3-dipolar cycloaddition, twofold extrusion, thioesters, organic azides, thiaziridines

Our ongoing interest in the organic chemistry of sulfur is focused on reactions of thiocarbonyl compounds with 1,3-dipoles [1–4]. Along with earlier studied dipoles such as nitrilium betaines, carbonyl- and thiocarbonyl ylides, azomethine ylides and diazo compounds, organic azides were used as reaction partners. Whereas some reactions with other dipoles occurred already at room temperature, those with organic azides needed more drastic conditions. In our hands, reactions with thioketones were performed conveniently using excess of an azide as the solvent. Thus, heating of 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**1**) in methyl azidoacetate led to a mixture of three products **2–4** [5] (Scheme 1). Similar treatment of **1** with benzyl azide yielded an imino compound **6** accompanied by "thiooxim ether" **5** [6].

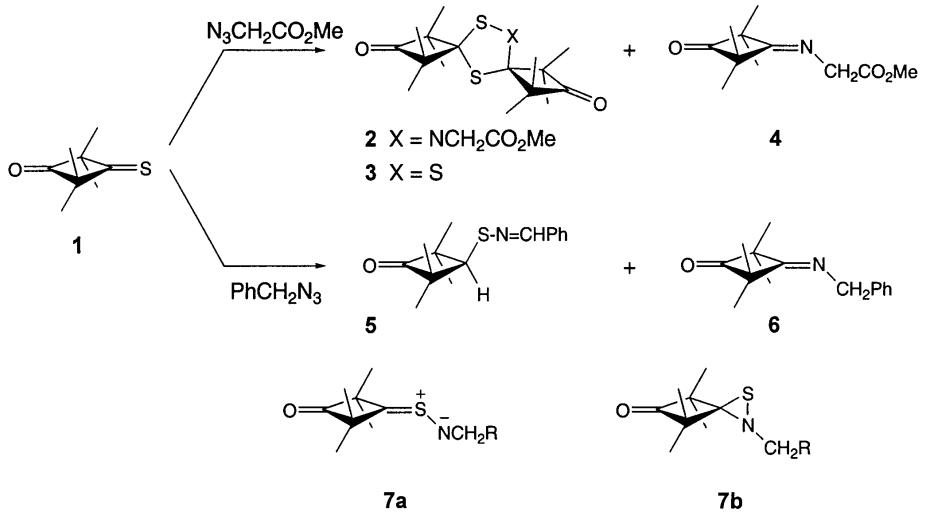
The formulation of the reaction mechanisms was based on the assumption of a 1,3-dipolar cycloaddition to give a 2,5-dihydro-1,2,3,4-thiatriazole derivative, which spontaneously eliminated N_2 generating thiocarbonyl S-imide **7a** as a reactive intermediate. The latter undergoes a cyclization to give a thiaziridine **7b** followed by sulfur extrusion (→ **4** ,**6**), a second cycloaddition (→ **2**), or an intramolecular 1,4-H shift (→ **5**)***.

When we started our investigations, only a few studies of transformations of thiocarbonyl compounds with azides had been published, and the synthetic potential

---

* Dedicated to Professor Alexander Senning on the occasion of his 65th birthday.
** Authors for correspondence.
*** For detailed studies on the structure and reactivity of thiocarbonyl S-imides see [7].

Scheme 1



of these reactions had not been explored. The only application was the preparation of imines from aromatic or sterically hindered thiocarbonyl compounds [8–10]. For this reason, we decided to involve in the study of reactions of thioesters and organic azides. Recently, reactions and synthetic applications of thiocarbonyl compounds were reviewed by Metzner [11].

RESULTS AND DISCUSSION

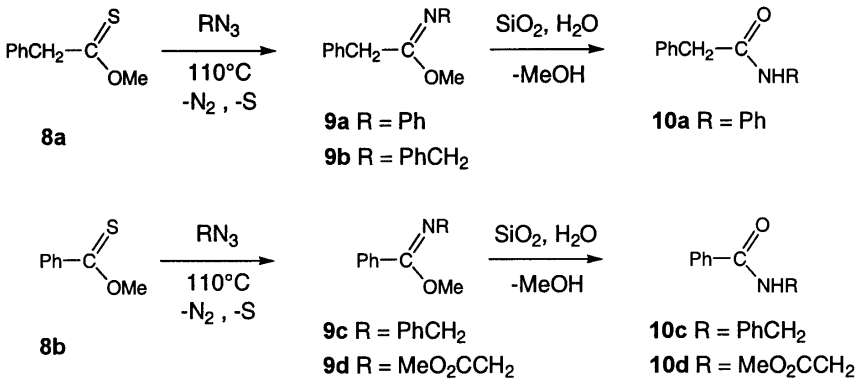
Compared with "monothione" **1**, thioesters and dithioesters are less reactive dipolarophiles [12]. Whereas reactions of azides with **1** were carried out at 80°C, similar reactions with thioesters required heating to 110°C. The reactions of phenyl azide with methyl mono- and dithiobenzoates leading to corresponding benzoic ester imides and benzoic thioester imides, respectively, were already reported [13].

The analogous reaction of O-methyl thiophenylacetate (**8a**) dissolved in phenyl azide led to the evolution ot N_2 and deposition of S_8. After removing of excess azide, a colorless oil was obtained and purified by distillation. The product was identified as methyl *N*-phenylimido benzoate (**9a**, Scheme 2). It showed a characteristic strong C=N absorption at 1670 cm^{-1}. In the ^{13}C-NMR spectra, the imidocarboxylate C-atom absorbed at 161.6 ppm*. Chromatographic purification (SiO_2, CH_2Cl_2) led to a color-

*Although **9a** and analogous products were "spectroscopically pure", no satisfying elemental analysis could be obtained.

less, crystalline product which was shown to be *N*-phenyl phenylacetamide (**10a**). Using the same thioester **8a** and benzyl azide, the primary crude product **9b** was isolated by distillation. Attempted purification on SiO_2 led to decomposition of **9b**.

Scheme 2



Similarly, the crude reaction product of a methyl thiobenzoate (**8b**) and benzyl azide* was chromatographed and *N*-benzyl benzamide (**10c**) was isolated as the final product. In the reaction of **8b** with methyl azidoacetate, distillation of the crude product yielded pure **9d**, which showed two equally strong absorption bands at 1750 and 1675 cm^{-1} for C=O and C=N, respectively. Correspondingly, absorption signals in the ^{13}C-NMR spectrum were found at 171.7 and 164.7 ppm and two signals for MeO at 3.87 and 3.71 ppm in the ^{1}H-NMR spectrum.

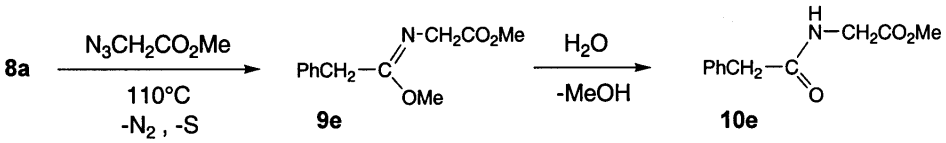
The formation of products **9** can be explained by the general mechanism formulated for the reactions of thiocarbonyl compounds with azides leading to imines [5,14]. The two key steps of this mechanism, the so-called "twofold extrusion" [15], are elimination of N_2 from the primarily formed 2,5-dihydro-1,2,3,4- thiatriazole to give a thiocarbonyl S-imide, followed by cyclization to thiaziridine and extrusion of sulfur.

An additional experiment carried out with methyl azidoacetate and O-methyl thiophenylacetate (**8a**) after typical workup afforded an oily product, which crystallized at room temperature. The ^{1}H-NMR spectra of the crude product, the product after distillation and the pure product after chromatography showed no significant differences; there was only one MeO signal present at 3.71 ppm accompanied by a singlet at 3.61 and a doublet at 3.97 ppm, each for one CH_2 group. The IR spectrum

*According to the ^{1}H-NMR spectra the crude product was **9c**; distillation led to the formation of a side product which might be a tautomer of **9c**.

showed two C=O absorption bands at 1730 and 1635 cm^{-1} and an NH band at 3140 cm^{-1}. These data confirm structure **10e** for this product (Scheme 3). In comparison with imines **9a–d**, the hydrolysis of **9e** is very fast and, therefore, it could not be isolated under the used conditions.

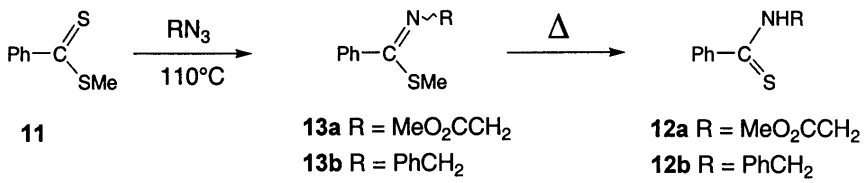
Scheme 3



An unexpected result was obtained in the reaction of methyl dithiobenzoate (**11**) and methyl azidoacetate at 110°C. Volumetric determination of the gaseous products showed that more than an equimolar amount of gas evolved. After cooling to room temperature, the volume was reduced due to condensation of one component, which was identified as dimethyl disulfide (b.p.108–110°C; GC, ^{1}H-NMR). According to the above described mechanism of imine formation and subsequent hydrolysis, the product was expected to be methyl *N*-benzoyl glycinate (**10d**, Scheme 2). But the isolated product, observed as the major component in the crude reaction mixture, showed the molecular formula $C_{10}H_{11}NO_2S$ (elemental analysis, MS). In the IR spectrum, an ester C=O band at 1750 cm^{-1} appeared, and the ^{13}C-NMR spectrum revealed the corresponding signal at 169.4 ppm. In addition, a singlet at 199.3 ppm indicated the presence of a thioamide function. On the basis of these data, the structure was established as the known *N*-thiobenzoyl glycinate (**12a**, Scheme 4) [16].

When the reaction mixture obtained in an analogous experiment was separated by distillation, the fraction obtained at 115–116°C/0.15 Torr (*ca.* 29%) was identified as an (*E/Z*)-mixture of thioimidate **13a** (Scheme 4). The ^{1}H-NMR spectrum of the crude reaction mixture before distillation revealed the presence of **12a** and **13a** in the ratio of *ca.* 2:1. After heating the mixture to 150°C for *ca.* 4 h, no **13a** could be detected (^{1}H-NMR). In contrast to experiments with thioester **8b** (Scheme 2), no deposition of elemental sulfur was observed after cooling of the mixture to room temperature.

Scheme 4



Reaction of **11** with benzyl azide (110°C, 8 h), after distillation led to a (*E/Z*)-mixture of thioimidate **13b** in 82% yield. The ^{1}H-NMR spectrum showed two MeS signals at 2.43 and 2.03 ppm as well as two CH_2 absorptions at 4.78 and 4.53 ppm. These data correspond to those reported by Walter and Meese [17]. When the reaction mixture obtained at 110°C was heated to 150°C for *ca*. 4 h, the (*E/Z*)-mixture of **13b** was completely converted into thioamide **12b**. Gaseous products formed in this reaction were bubbled through CCl_4 and the CCl_4-solution was analyzed by ^{1}H-NMR spectroscopy; dimethyl disulfide was identified as a product.

In order to get more insight into the reaction course of this unexpected conversion, a mixture of isolated **13b** and one mol-equivalent of S_8 was heated to 180°C. After completion of the reaction, thioamide **12b** and dimethyl disulfide were identified as major products. Based on these observations we concluded that the formation of **12** from **11** proceeds *via* the initial product **13**. In the analogous reactions with **8b** (Scheme 2), sulfur crystallizes from the mixture; in the case of **11** sulfur formed *in situ* is involved in the transformation of the initial product **13** into **12**. The source of sulfur in reactions of thiocarbonyl compound with azides is an intermediate thiaziridine [14].

Although the presented experiments show that thioamides **12** are formed *via* intermediate thioimidates **13**, the reaction mechanism involving elemental sulfur is still unknown. With the aim of testing the ability of other sulfurization reagents to convert thioimidates of type **13** into thioamides **12**, a sample of **13b** and ammonium polysulfide ($(NH_4)_2S_X$) in ethanol was refluxed for one hour. After this time, no **13b** could be detected in the mixture, and thioamide **12b** was isolated in 45% yield after crystallization [18].

In summary, we showed that reactions of organic azides with thio- and dithiocarboxylates offer an alternative approach to imidates and thioimidates, respectively. Both types of compounds are useful starting materials in heterocyclic chemistry (*e.g.* [19–21]). The derivatives obtained from the reactions with azidoacetates found relevant applications in amino acid chemistry [22–23]. Elemental sulfur was shown to be an efficient agent for the demethylation of CH_3S groups of thioimidates and to convert them into thioamides. The mechanism of this unexpected reaction is not clear and requires further studies.

EXPERIMENTAL

General. M.p's were determined in a capillary using a MEL-TEMP II (Aldrich) apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were registered with a Varian Gemini-200 BB (200 MHz for ^{1}H and 50 MHz for ^{13}C) spectrometer in $CDCl_3$ solutions using TMS as an internal standard (δ_{TMS} = 0 ppm). IR-spectra were recorded with a Specord 75-IR spectrometer. MS-spectra were registered with an LKB-2092 or a Varian MAT-1125 spectrometer using either Cl (with NH_3) or EI (70 eV) mode. Starting materials were prepared according to known protocols: phenyl azide [24], benzyl azide [25], methyl azidoacetate [5], O-methyl thiobenzoate [26], methyl dithiobenzoate [27], O-methyl phenylthioacetate [26,28], and ammonium polysulfide [29].

Reactions of azides with O-methyl thioesters 8a,b. – *General procedure*. Solutions of 3.0 mmol of **8** in 1.0 ml of the respective azide were stirred magnetically in an oil bath at 110°C. Evolution of N_2 was monitored using a gas-burette connected with the reaction flask. After 6–8 h, evolution of N_2 ceased, and the amount of evolved N_2 approximately corresponded to the expected volume (*ca*. 75 ml). The solutions were stored in the refrigerator overnight and elemental sulfur precipitated was filtered. Excess azide was removed from the clear mixture by distillation (Kugelrohr; 50–60°C/10^{-1} Torr). The oily thick residues were examined by ^{1}H-NMR and IR spectra and were purified by distillation *in vacuo* (bulb-to-bulb). Comparison of the IR spectra taken before and after distillation revealed no significant differences (only traces of contaminating azide were removed). Reported yields relate to amounts of distilled products.

Methyl N-*(Phenyl)phenylacetimidate* (**9a**). Colorless, thick oil, distilled at 95–100°C/10^{-3} Torr. Yield: 460 mg (68%) (ref. [30]: b.p. 110–112°C/3·10^{-1} Torr). ^{1}H-NMR: 7.25–7.05, 6.95–6.65 (2*m*, 10 arom. H); 3.75 (*s*, MeO); 3.47 (*s*, CH_2). ^{13}C-NMR: 161.6 (C=N); 148.5, 135.7 (2*s*, 2 arom. C); 128.9, 128.8, 128.4, 126.5, 122.9,121.3 (6*d*, 10 arom. CH); 53.4 (*q*, MeO); 35.9 (*t*, CH_2). IR (film): 1670*vs* (C=N), 1495*m*, 1435*m*, 1290*s* (br.), 1245*vs* (MeO), 1185*s*, 1035*m*, 770*vs*, 740*vs*, 705*vs*.

Methyl N-*(Benzyl)phenylacetimidate* (**9b**). Colorless, thick oil, distilled at 145–150°C/2·10^{-1} Torr. Yield: 531 mg (74%). ^{1}H-NMR: 7.30–7.10 (*m*, 10 arom. H); 4.50 (*s*, CH_2N); 3.70 (*s*, MeO); 3.60 (*s*, CH_2). ^{13}C-NMR: 162.5 (C=N);140.8, 135.5 (2*s*, 2 arom. C); 128.6, 128.5, 127.9, 127.1, 126.9, 126.4 (6*d*, 10 arom. H); 52.7 (*t*, CH_2N); 52.1 (*q*, MeO); 35.4 (*t*, CH_2).

Methyl N-*Benzylbenzimidate* (**9c**). Colorless, thick oil, distilled at 106–110°C/2·10^{-1} Torr. Yield: 439 mg (65%) (ref. [22]: b.p. 105–108°C/10^{-2} Torr). ^{1}H-NMR: 7.45–7.35, 7.30–7.20 (2*m*, 10 arom. H); 4.52 (*s*, CH_2); 3.87 (*s*, MeO). IR (film): 1680*vs* (C=N), 1450*s* (br.), 1285*vs* (MeO), 1205*m*, 1130*s*, 1090*m*, 1040*m*, 780*m*, 745*vs*, 710*vs*.

Methyl N-*(α-Methoxybenzylidene)glycinate* (**9d**). Colorless, thick oil, distilled at 90–95°C/10^{-1} Torr. Yield: 560 mg (90%) (ref. [22]; b.p. 90–91°C/10^{-2} Torr). ^{1}H-NMR: 7.45–7.30 (*m*, 5 arom. H); 4.10 (*s*, CH_2); 3.87, 3.71 (2*s*, 2 MeO). ^{13}C-NMR: 171.7, 164.7 (2*s*, C=O, C=N); 131.5 (*s*, 1 arom. C); 129.9, 128.5, 127.8 (3*d*, 5 arom. CH); 53.5, 52.0 (2*q*, 2 MeO); 51.8 (*t*, CH_2). IR (film):1750*vs* (C=O), 1675*vs* (C=N), 1445*s*, 1300*vs* (br.), 1200*vs* (br.), 1140*s*, 1100*m*, 785*m*, 720*vs*.

Conversion of imidoesters 9a and 9c to N-substituted amides 10a and 10c. A solution of imidoester **9** (1 mmol) in CH_2Cl_2 was passed through a SiO_2 column. Analytical pure samples were obtained after recrystallization from Et_2O. Reported yields refer to products isolated from the column.

N-*(Phenyl)phenylacetamide* (**10a**). Colorless crystals, m.p. 112–114°C. Yield: 185 mg (88%) (ref. [31]: m.p. 112–114°C). IR (KBr): 3320*m* (NH), 1650*vs* (C=O), 1600*s*, 1550*m*, 1495*m*, 1440*s*, 760*s*, 730*s*, 700*s*.

N-*Benzylbenzamide* (**10c**). Colorless crystals, m.p. 101–103°C. Yield: 199 mg (94%) (ref. [32]: m.p. 102–105°C). IR (KBr): 3230*s* (NH), 1640*vs* (C=O), 1550s,1325m, 740*s*, 705*vs*.

Reaction of 8a with methyl azidoacetate. A solution of 332 mg (2 mmol) **8a** in 1.0 ml (1.22 g, 10.6 mmol) methyl azidoacetate was magnetically stirred and heated to 110°C (oil bath) for 4.5 h. Excess of methyl azidoacetate was removed at 50°C/10^{-1} Torr, and the thick residue was distilled at 120–130°C/10^{-3} Torr to give a colorless oil which crystallized at room temperature within a few hours. Instead of distillation, chromatography (SiO_2, CH_2Cl_2/MeOH 96:4) could be applied. An analytically pure sample of **10e** was obtained by recrystallization from diisopropylether with small amounts of CH_2Cl_2.

Methyl N-*(Phenylacetyl)glycinate* (**10e**). Colorless prisms, m.p. 84–86°C. Yield (after chromatography and crystallization):170 mg (41 %) (ref. [33]: m.p. 89–90°C). IR (KBr): 3250*m* (NH), 1730*vs* (C=O ester), 1635*s* (C=O amide), 1555*s*, 1410*m*, 1365*m*, 1210*s*, 720*m*.

Reaction of 11 with methyl azidoacetate. A red solution of 505 mg (3 mmol) **11** in 1 ml (1.22 g, 10.6 mmol) methyl azidoacetate was magnetically stirred and heated to 110°C (oil bath) for 6 h. There were *ca*. 95 ml of gases collected in the burette (expected amount of N_2 *ca*. 75 ml). After removing of excess methyl) azidoacetate (50°C/10^{-1} Torr), the red-brown residue was distilled at 120–125°C/1.5·10^{-1} Torr to give 607 mg of an oily, colorless product which was identified as a *ca*. 1:1 mixture of (*Z*)- and (*E*)-thioimidate **13a** contaminated with *ca*. 20% of **12a**. Repeated distillation afforded an almost pure 1:1 mixture of (*Z*)- and (*E*)-**13a**.

Methyl N-*[α-(Methylsulfanyl)benzylidene]glycinate* (**13a**) (*ca*. 1:1 mixture of (*Z*)- and (*E*)-isomers). Colorless, thick liquid, distilled at 115–116°C/1.5·10^{-1} Torr. Yield: 201 mg (30%) (ref. [16]: b.p. 115–116°C/2·10^{-2} Torr). ^{1}H-NMR: 4.42, 4.12 (2*s*, 2 CH_2); 3.75, 3.67 (2*s*, 2 MeO); 2.43, 2.09 (2*s*, 2 MeS).

When the heating was continued for another 4 h at 150°C, after removing of methyl azidoacetate, crystallization of the oily residue afforded **12a** as the exclusive product.

Methyl N-*(Thiobenzoyl)glycinate* (**12a**). Bright yellow crystals, m.p. 69–70°C (petroleum ether). Yield: 521 mg (83%) (ref. [34]: m.p. 70–71°C). ^{1}H-NMR: 8.40 (br. *s*, NH); 7.81–7.78, 7.77–7.74, 7.51–7.30 (3*m*, 5 arom. H); 4.52 (*d*, *J* = 4.75 Hz, CH_2); 3.79 (*s*, MeO). ^{13}C-NMR: 199.3 (*s*, C=S); 169.4 (*s*, C=O); 140.7 (*s*, 1 arom. C); 131.4, 129.1, 128.9, 128.5, 126.8 (5*s*, 5 arom. CH); 52.7 (*q*, MeO); 47.8 (*t*, CH_2). IR (KBr): 3230*m* (NH), 1750*vs* (C=O), 1440*s*, 1215*vs*, 760*m*, 710*s*. Anal. Calc. for $C_{10}H_{11}NO_2S$ (209.27): C 57.40, H 5.30, N 6.69. Found: C 57.37, H 5.33, N 6.69.

Reaction of 11 with benzyl azide. A solution of 505 mg (3 mmol) **11** in 1 ml (1070 mg, 8.0 mmol) benzyl azide was magnetically stirred and heated to 110°C (oil bath). After 8 h, N_2 evolution was complete, and the reaction mixture was stored overnight in the refrigerator. The yellow precipitate of S_8 was filtered, and the clear solution was heated in a Kugelrohr at 50°C/1.5·10^{-1} Torr to remove excess benzyl azide. The residual oil was distilled at 120–125°C/1.5·10^{-1} Torr to give 607 mg (82%) of an almost pure mixture of (*Z*)- and (*E*)-isomers of **13b** ((*Z*/*E*) ratio *ca*. 1:1, ^{1}H-NMR).

Methyl N-*(Benzyl)thiobenzimidate* (**13b**). Colorless, thick oil, distilled at 120–125°C/1.5·10^{-1} Torr. Yield: 594 mg (82%) (ref. [35]: b.p. 181°C/2.5 Torr). ^{1}H-NMR: 7.50–7.17 (*m*, 10 arom. H); 4.78, 4.53 (2*s*, 2 CH_2); 2.43, 2.08 (2*s*, 2 MeS).

After 8 h at 110°C, the temperature of the oil-bath was raised to 180°C and stirring was continued for 4 h. After removing of excess benzyl azide, the residue solidified and crystallization from petroleum ether yielded bright yellow crystals which were identified as thioamide **12b**.

N-*(Benzyl)thiobenzamide* (**12b**). Bright yellow crystals, m.p. 85–86°C (petroleum ether). Yield: 566 mg (83%) (ref. [37]: m.p. 86°C). ^{1}H-NMR: 7.40–7.10 (*br. s*,10 arom. H); 4.92 (*d*, *J* = 5.5 Hz, CH_2). ^{13}C-NMR: 199.7 (*s*, C=S); 142.0, 136.7 (2*s*, 2 arom. C); 131.3, 129.3, 128.8, 128.6, 128.4, 127.2 (6*d*,10 arom. CH); 51.0 (*t*, CH_2).

Reaction of 13b with elemental sulfur. A round-bottom flask, containing 241 mg (1 mmol) of **13b** and 256 mg (1 mmol) of S_8 and equipped with a magnetical stirrer, was closed with a bubbling cap filled with 2 ml of CCl_4. The mixture was heated to 180°C (oil bath) and gaseous products were passed through the CCl_4. After 8 h, the reaction was completed and the CCl_4-solution was examined by ^{1}H-NMR. A singlet at 2.38 ppm revealed the presence of dimethyl disulfide (no difference of the spectrum after addition of a small amount of an original sample of CH_3S-SCH_3). The reaction mixture was cooled to room temperature, 10 ml of diethylether were added and the yellow precipitate of S_8 was filtered. Evaporation of the solvent and recrystallization of the residue from petroleum ether afforded 209 mg (92%) of bright yellow crystals of **12b**.

Reaction of 13b with ammonium polysulfide [18]. To a solution of 350 mg (1.45 mmol) **13b** in 4 ml ethanol, 580 mg (*ca*. 3 mmol) of ammonium polysulfide (being mainly ammonium pentasulfide) were added, and the mixture was refluxed for 1 h. Ethanol was evaporated, and the residue was treated with 20 ml CH_2Cl_2 and filtered to remove undissolved solid. The solvent was evaporated, and the yellow residue was crystallized from CH_2Cl_2 to give a crystalline, bright yellow solid with m.p. 87–88.5°C, which was identified as *N*-(benzyl)thiobenzamide (**12b**; ^{1}H-NMR, IR, no changes of m.p. when mixed with authentic **12b**).

Acknowledgment

We thank the Polish State Committee for Scientific Research (Grant No. 3 TO9A 007 16), the Swiss National Science Foundation and F. Hoffmann-La Roche AG, Basel, for financial support. Technical assistance by Mrs. M. Celeda is gratefully acknowledged.

REFERENCES

1. Heimgartner H., *Phosporus, Sulfur and Silicon*, **58**, 281 (1991).
2. Mlostoń G., Romański J., Kägi M. and Heimgartner H., *Polish J. Appl. Chem*., **41**, 361 (1997).
3. Mlostoń G., *Phosphorus, Sulfur and Silicon*, **153**, 217 (1999).
4. Mlostoń G. and Heimgartner H., *Polish J. Chem*., **74**, 1503 (2000).
5. Mlostoń G., Romański J., Linden A. and Heimgartner H., *Polish J. Chem*., **70**, 880 (1996).
6. Mlostoń G., Romański J., Linden A. and Heimgartner H., *Helv. Chim. Acta*, **78**, 1067 (1995).
7. Fabian J. and Mlostoń G., *Polish J. Chem*., **73**, 669 (1999); Mlostoń G. and Fabian J., *Polish J. Chem*., **73**, 683 (1999).
8. Schönberg A. and Urban W., *J. Chem. Soc*., 530 (1935).
9. Guziec F.S. and Moustakis Ch., *J. Chem. Soc., Chem. Commun*., 63 (1984).
10. Pekcan S. and Heimgartner H., *Helv. Chim. Acta*, **71**, 1673 (1988).
11. Metzner P., *Topics Curr. Chem*., **204**, 127 (1999).
12. Huisgen R. and Li X., *Tetrahedron Lett*., **24**, 4185 (1983).
13. Mlostoń G., Romański J., Linden A. and Heimgartner H., *Helv. Chim. Acta*, **78**, 1499 (1995).
14. Mlostoń G., *Chem. Papers*, **52**, 56 (1998).
15. Guziec F.S. and Sanfilippo L.J., *Tetrahedron*, **44**, 6241 (1988).
16. Bachi M.D. and Rothfield M., *J. Chem. Soc., Perkin Trans. 1*, 2326 (1972).
17. Walter W. and Meese C.O., *Chem. Ber.*, **109**, 922 (1976).
18. Depczynski R., Diploma thesis, University of Łódź, 2000.
19. a) Pielartzik H., Irmisch-Pielartzik B. and Eicher T., in "Methoden der organischen Chemie (Houben-Weyl)", Band E5/1, ed. Falbe J., Thieme Verlag, Stuttgart,1985, p. 812; b) Bauer W. and Kühlein K., *ibid*., Band E5/2, p. 931.
20. Bellassoued M., Gaudemar M., Hajjem B. and Baccar B., *Bull. Soc. Chim. Belg*., **95**, 65 (1986).
21. Padwa A., Gasdaska J.R., Hoffmann G. and Rebello H., *J. Org. Chem*., **52**, 1027 (1987).
22. Schulthess A.H. and Hansen H.-J., *Helv. Chim. Acta*, **64**, 1322 (1981).
23. Hiroi K., Hidaka A., Sesaki R. and Iwamura Y., *Chem. Pharm. Bull. Jpn*., **45**, 769 (1997).
24. Ugi I., Perlinger H. and Behringer L., *Chem. Ber.*, **91**, 2330 (1958).
25. Maier G., Eckwert J., Bothur A., Reisenauer H.P. and Schmidt Ch., *Liebigs Ann. Chem*., 1041 (1996).
26. Pedersen B.S., Scheibye S., Clausen K. and Lawesson S.-O., *Bull. Soc. Chim. Belg*., **87**, 293 (1978).
27. Davy H., *J. Chem. Soc., Chem. Commun*., 457 (1982).
28. Mayer R., Scheithauer S. and Kunz D., *Chem. Ber.*, **99**, 1393 (1966).
29. Supniewski J., Preparation of Inorganic Compounds, PWN, Warszawa 1958, p. 412 (in Polish).
30. Raap R., *Can. J. Chem*., **49**, 1792 (1971).
31. Metz P. and Mues C., *Tetrahedron*, **44**, 6841 (1988).
32. Knowles H.S., Parson A.F., Pettiter R.M. and Rickling S., *Tetrahedron*, **56,** 979 (2000).
33. Williams A., Lucas E.C., Rimmer A.R. and Hawkins H.C., *J. Chem. Soc., Perkin Trans. 2*, 627 (1972).
34. De Bruin K.E. and Boros E.E., *J. Org. Chem*., **55**, 6091 (1990).
35. Boudet R., *Ann. Chim. (Paris)*, **10**, 178 (1955); *Chem. Abstr.*, **50**, 4055a (1956).
36. Sasaki Y. and Olsen F.P., *Can. J. Chem*., **49**, 271 (1971).