5-Morpholino-1,2,3,4-thiatriazole as a Sulfur-Transfer reagent in the reactions with Thioketones

Mlostoń, Grzegorz ; Woźnicka, M ; Heimgartner, H

Abstract: The thermal decomposition of 5-morpholino-1,2,3,4-thiatriazole (7), which leads to the extrusion of an active form of sulfur, in the presence of different thioketones is described. The interception of the S-atom by the C=S bond leads to in situ formation of an elusive thiocarbonyl S-sulfide of type 5. This intermediate is a prone 1,3-dipole, which undergoes effectively [2+3] cycloadditions with thioketones to yield 1,2,4-trithiolane derivatives in a regioselective manner. Unexpectedly, 3,3-dichloro-2,2,4,4-tetramethyl-3-thioxocyclobutanone (1c) does not lead to the expected symmetrical 1,2,4-trithiolane. This result can be explained by the reduced stability of the corresponding thiosulfine 5c. Three-component reactions, which were carried out in the presence of equimolar amounts of two different thioketones, result in the formation of 'mixed' 1,2,4-trithiolanes of type 8.

DOI: https://doi.org/10.1002/hlca.200790060

Prof. Dr. H. Heimgartner
Tel. 01 635 4282
Fax 01 635 6812
e-mail: heimgart@oci.unizh.ch

5-Morpholino-1,2,3,4-thiatriazole as a Sulfur-Transfer Reagent in the Reactions with Thioketones

by **Grzegorz Mloston**[*] and **Marta Woznicka**[1])

University of Lodz, Department of Organic and Applied Chemistry, Narutowicza 68, PL-90-136 Lodz
(phone: +48 42 635 5761; fax: +48 42 635 5380; e-mail: gmloston@uni.lodz.pl)

and

Heinz Heimgartner[*]

Organisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich
(phone: +41 44 635 4282; fax: +41 44 635 6812; e-mail: heimgart@oci.unizh.ch)

[1]) Part of the planned Ph. D. thesis of *M. W.,* University of Lodz.

The thermal decomposition of 5-morpholino-1,2,3,4-thiatriazole (**7**), which leads to the extrusion of an active form of sulfur, in the presence of different thioketones is described. The interception of the S-atom by the C=S-bond leads to *in situ* formation of an elusive thiocarbonyl *S*-sulfide of type **5**. This intermediate is a prone 1,3-dipole, which undergoes effectively [2+3]-cycloadditions with thioketones to yield 1,2,4-trithiolane derivatives in a regioselective manner. Unexpectedly, 3,3-dichloro-2,2,4,4-tetramethyl-3-thioxocyclo-butanone (**1c**) does not form the expected symmetrical 1,2,4-trithiolane. This result can be explained by the reduced stability of the corresponding thiosulfine **5c**. Three-component reactions, which were carried out in the presence of equimolar amounts of two different thioketones, result in the formation of 'mixed' 1,2,4-trithiolanes of type **8**.

1. Introduction. – Sulfur-transfer reactions have been reported frequently in recent years [1][2]. The C,S-double bonds of thioketones are prone interceptors of sulfur, and thiocarbonyl *S*-sulfides ('thiosulfines') are believed to be formed as the reactive intermediates. They can be trapped efficiently with dipolarophiles, and in the case of the thiocarbonyl group, the [2+3]-cycloaddition leads to 1,2,4-trithiolanes [3–7]. In these sulfur-transfer reactions, strained three-membered sulfur heterocycles such as thiiranes [3], or *in situ* formed thiaziridines [4][5] or oxathiiranes [6][7] are the sulfur donors. The appearance of thiaziridines as intermediates was proposed for the reactions of thiocarbonyl compounds with organic azides, which are initiated by the [2+3]-cycloaddition to give 2,5-dihydro-1,2,3,4-thiatriazoles, followed by extrusion of N_2. A typical example with adamantanethione (**1a**) and PhN_3 is presented in *Scheme 1* [5].

Scheme 1

On the other hand, some S-containing five-membered heterocycles, which are stable at room temperature, are reported to undergo thermal or photochemical decomposition under S-extrusion, *e.g.*, 1,3,4-oxathiazol-2-ones decomposed in boiling xylene in the presence of **1a** to give **6a** in moderate yield [8]. In this case, a thiazirine is believed to act as the S-donor. Similarly, the photochemical decomposition of the same type of precursor at 10K was reported to yield phenyl thiazirine, which upon warming isomerized to benzonitrile sulfide. Finally, the latter decomposed to give benzonitrile and sulfur [9]. Analogous intermediates were detected in the photochemical reactions of 5-phenyl-1,2,3,4-thiatriazole and 5-phenyl-1,2,3,4-thiatriazole-2-thione [9].

The thermal decomposition of easily available 5-amino-1,2,3,4-thiatriazoles was studied by *Neidlein* and *Tauber* [10]. The formation of phenyl cyanamide was proposed to occur *via* a thiazirine intermediate. Therefore, the final product is formed *via* a stepwise elimination of N_2 and S. On the other hand, *Wentrup et al.* claimed that the thermal decomposition of 5-phenyloxy-1,2,3,4-thiatriazole occurs by elimination of the labile N_2S [11]. This interpretation was adopted by *Adam* and *Bargon* to explain the S-transfer from the same precursor to strained cycloalkenes leading to the corresponding thiiranes ('episulfidation') [12].

The successful 'episulfidation' of strained alkenes with 5-aryloxy-1,2,3,4-thiatriazoles prompted us to examine possible applications of analogous reactions with 5-morpholino-1,2,3,4-thiatriazole (**7**), which is more convenient in its handling, as a sulfur donor in reactions with thioketones. The study was aimed at the examination of a new method for the generation of thiocarbonyl *S*-sulfides as reactive intermediates. As potential S-acceptors, the aliphatic thioketones **1a**–**1d** as well as the aromatic thioketones **1e** and **1f** were used.

Formulae **1a**–**1f**

Furthermore, the proposed equilibrium between 'thiosulfine' and dithiirane, which has been discussed in recent papers [1][13–15], was of interest.

2. Results and Discussion. – The crystalline precursor **7** was prepared from morpholine, thiophosgene ($Cl_2C=S$), and NaN_3 without isolation of the intermediate

thiocarbamoyl chloride, in analogy to other 1,2,3,4-thiatriazole derivatives (for other preparations see [16][17]). When heated to *ca.* 115° (m.p.), **7** decomposed with N_2 evolution and formation of elemental S. Therefore, the reactions with thioketones were performed in boiling toluene. Under these conditions, the decomposition was complete after *ca.* 2 h.

The reaction of **7** with adamantanethione (**1a**) gave the known symmetrical 1,2,4-trithiolane **6a** in moderate yield. Similarly, 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**1b**) was smoothly converted into the known trithiolane **6b** (Scheme 2)[2]). In contrast, the attempted transformations of 3,3-dichloro-2,2,4,4-tetramethylcyclobutanethione (**1c**) as well as of diisopropylthioketone (**1d**) were in vain.

Scheme 2

Heating of **7** in the presence of a mixture of equimolar amounts of **1a** and **1b** led to three different 1,2,4-trithiolanes, *i.e.*, the symmetrical **6a** and **6b** along with the unsymmetrical **8a** (45% yield) in a *ca.* 1:1:2 ratio (*Scheme 3*). An analogous experiment, in which **1b** was replaced by **1c**, led to the symmetrical trithiolane **6a** exclusively, and the unconverted thioketone **1c** remained in the mixture (^{1}H-NMR). It is worth mentioning that the same result was obtained, when a mixture of **1a** and **1c**, dissolved in excess PhN_3, was heated

[2]) The trithiolane **6b** was also obtained (60%) when a solution of **1b** in xylene was heated in the presence of S_8 under reflux according to the protocol described in [18].

to 80°. In this system, the intermediate thiaziridine of type **3** is believed to be the S-donor (*cf.* [5] and *Scheme 1*)[3]).

Scheme 3

An aromatic thioketone, *i.e.*, thiobenzophenone (**1e**), was used in the three-component reaction with **7** and **1b**. In this case, the formation of the mixed trithiolane **8b** was the sole product (*Scheme 4*). This result corresponds with an earlier observation, when **8b** was formed in the three-component reaction of PhN_3 with a mixture of thioketones **1b** and **1e** [4]. Similarly, heating of a solution of **7** and an equimolar mixture of **1c** and **1e** in toluene resulted in the formation of the corresponding mixed trithiolane **8c**. In both cases, the crystalline trithiolanes were isolated in 50–60% yield.

Scheme 4

The reactivity of 9*H*-fluorene-9-thione (**1f**) exceeds that of thiobenzophenone (**1e**) toward 1,3-dipoles, but it is thermally less stable and undergoes easily dimerization in terms of a [2+4]-cycloaddition [20]. Probably for this reason, no interception product, neither symmetrical nor mixed trithiolanes, were formed in the experiment with **1c**, **1f** and **7**.

---

[3]) Heating of a mixture of **1a** and *N*-methyl benzylidenamine in PhN_3 at 80° led to **6a**, *N*-methyl thiobenzamide, and *N*-methyl adamantan-2-ylidenamine. Thus, **1a** as well as the benzaldimine act as S-acceptors, and a thiaziridine was proposed as the S-donor [19].

The formation of the 1,2,4-trithiolane is the result of a [2+3]-cycloaddition of the respective thioketone and the *in situ* formed thiocarbonyl *S*-sulfide ('thiosulfine') [3]. In the reactions reported in the present paper, the thermolabile 5-morpholino-1,2,3,4-thiatriazole (**7**) acts as the S-donor. In the light of the literature data, two pathways for the S-transfer reaction can be discussed. Whereas photochemical decompositions of 1,2,3,4-thiatriazoles occur via N_2 elimination, leading to a thiazirine/nitrile sulfide system [9][10], thermolysis results in the fragmentation to give N_2S and the nitrile [11]. It is likely that the type of substituent at C(5) of the 1,2,3,4-thiatriazole influences the mode of decomposition and, thereby, the type of the active S-donor. The reaction conditions applied in the present study favor rather the pathway *via* N_2S elimination.

In accordance with previous observations, thioketones in general are good interceptors for the S-atom delivered during decomposition of **7**. Once again, adamantanethione (**1a**) acted as a superior acceptor leading to the thiocarbonyl *S*-sulfide **5**, which in turn easily underwent a [2+3]-cycloaddition with the C=S group to give the corresponding 1,2,4-trithiolane.

The second-efficient S-acceptor of the selected thioketones was 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**1b**). On the other hand, its 3,3-dichloro derivative **1c** and diisopropylthioketone (**1d**) were not able to form a sufficiently stable thiocarbonyl *S*-sulfide, which could undergo the [2+3]-cycloaddition with the C=S bond.

The astonishing difference in the behavior of **1b** and **1c** suggests that the stability and/or reactivity of the corresponding *S*-sulfides are influenced by the substitution pattern. The enhanced stability of the intermediate derived from **1b** can result from a stabilizing transannular interaction with the C=O group (*cf.* [21]).

In none of the studied systems was the presence of a dithiirane evidenced. Obviously, the intermediate thiocarbonyl *S*-sulfides either undergo a [2+3]-cycloaddition or decompose to give the parent thioketone.

The results of the three-component reactions with thiobenzophenone (**1e**) and **1b** or **1c** deserve a short comment. The formation of **8b** results either from the interception of thiobenzophenone *S*-sulfide (**5f**) with **1b** or of 2,2,4,4-tetramethyl-3-thioxocyclobutanone *S*-sulfide (**5b**) with **1e**. The absence of the symmetrical 1,2,4-trithiolane **6b** and 2,2,4,4-tetraphenyl-1,2,4-trithiolane can be explained by the fact that tetraaryl-substituted trithiolanes are thermally unstable and, under the reaction conditions, easily undergo the [2+3]-cycloreversion [3]. On the other hand, if the *S*-sulfide **5b** should be formed, it would react preferably with the 'superdipolarophile' **1e** to give **8b**.

Scheme 5

As it was shown that **1c** does not form the expected symmetrical 1,2,4-trithiolane of type **6**[4]), the formation of **8c** in 52% yield is most likely the result of the [2+3]-cycloaddition of **5f** with **1.**

The authors thank Mrs. *Malgorzata Celeda* (University of Lodz) for superior technical assistance. *G. M.* acknowledges financial support by the *Polish State Committee for Scientific Research* (Grant No. 4T09A 046 25) and *H. H.* thanks *F. Hoffmann-La Roche AG,* Basel, for financial support. We also thank Dr. *H. Petzold* for the optimization of the synthesis of **6b** from **1b** and elemental sulfur.

Experimental Part

1. *General*. M.p.'s were determined in capillary using a *Meltemp 2* apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were registered with a *Tesla BS 687* (80 and 20 MHz, resp.) or a *Bruker 300* (300 and 75 MHz, resp.) spectrometer using TMS ($\delta_{TMS} = 0$ ppm) as an internal standard. IR spectra were taken in KBr pellets with a *Nexus* spectrophotometer. CI-MS were registered on a *Finnigan-Mat-90* or *Finnigan-SSQ-700* spectrometer. Elemental analyses were performed in the Analytical Laboratory of the University of Zurich.

---

[4]) However, heating of **1c** in excess PhN_3 at 80° gave this trithiolane in 36% yield [22]. Remarkably, no interception of the proposed thiocarbonyl *S*-imide with **1c** was observed (for comparison see [23]).

2. *Starting materials*. 3,3-Dichloro-2,2,4,4-tetramethylcyclobutanethione (**1c**) [22], adamantanethione (**1a**) [24], and 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**1b**) [25] were prepared from the corresponding ketones by thionation with P_4S_{10} in pyridine solution. 2,4-Dimethylpentane-3-thione (**1d**) [26] and 9*H*-fluorene-9-thione (**1f**) [27] were prepared by treatment of the corresponding ketones with a mixture of HCl and H_2S in MeOH, in the presence of catalytic amounts of $HC(OCH_3)_3$. Thioketone **1d** was purified by column chromatography (CC) on SiO_2. Thiobenzophenone (**1e**) was obtained by thionation of benzophenone with *Lawesson*'s reagent in boiling toluene [20]. *5-Morpholine-1,2,3,4-thiatriazole* (**7**) was obtained from morpholine-4-carbothioyl chloride (synthesized from $Cl_2C{=}S$ and morpholine according to [28]) and NaN_3. The crude morpholine-4-carbothioyl chloride was stirred with two equivalents of NaN_3 in acetone at r.t. for 19 h to afford colorless crystals; overall yield 58%; m. p. 109–112° (hexane/CH_2Cl_2) ([16][17]: 114–115°).

3. *Synthesis of Trithiolane* **6b** *from* **1b** *and Elemental Sulfur*. To a soln. of **1b** (156 mg, 1 mmol) in xylene (1 ml) was added S_8 (128 mg, 0.5 mmol). After heating to reflux, the yellow solid dissolved completely, and heating was continued for 75 h. The soln. was evaporated to dryness i.v. using a Kugel-Rohr apparatus and the crude product was dissolved in Et_2O to separate residual S_8. The Et_2O was evaporated and the product was purified by crystallization from hexane to yield 103 mg (60%) of *1,1,3,3,7,7,9,9-Octamethyl-5,10,11-trithiadispiro[3.1.3.2]undecane-2,8-dione* (**6b**). Colorless crystals; m.p. 88–92° ([29]: 100–102°).

The attempted analogous synthesis of the corresponding symmetrical 1,2,4-trithiolane from **1c** and S_8 in toluene at 120° was in vain. After heating for 50 h, no traces of the expected trithiolane were detected in the mixture (^{1}H-NMR).

4. *Two-Component Reactions of* **7** *with Thioketones.* A soln. of **7** (218 mg, 1 mmol) and 2 mmol of the corresponding thioketone **1** in 1 ml of toluene was stirred for 2 h at 120° (oil bath). After evaporation of the solvent, trithiolanes **6** were isolated either by crystallisation (**6a**) or after prep. TLC using plates precoated with SiO_2 (**6b**).

Dispiro[adamantane-2,2'-[1,2,4]trithiolane-5',2"-adamantane] (**6a**). Yield: 140 mg (38%). Colorless crystals. M.p. 195–200° (hexane/CH_2Cl_2) ([30]: 203–205°).

1,1,3,3,7,7,9,9-Octamethyl-5,10,11-trithiadispiro[3.1.3.2]undecane-2,8-dione (**6b**). Yield: 132 mg (38%). Colorless crystals. M. p. 97–101° (MeOH/CH_2Cl_2) ([29]: 100–102°).

5. *Three-Component Reactions of* **7** *with Thioketones*. A soln. of **7** (218 mg, 1 mmol) and two thioketones (1 mmol each) in 1 ml of toluene was stirred for 2 h at 120° (oil bath). Then, the solvent was evaporated and the mixture was separated by prep. TLC. Pure products **6** and **8** were obtained by subsequent crystallisation.

Reaction of **7**, **1a**, and **1b**. *Dispiro[adamantane-2,2'-[1,2,4]trithiolane-5',2"-adamantane]* (**6a**). Yield: 75 mg (41%). Colorless crystals. M.p. 195–200° (hexane/CH_2Cl_2) ([29]: 203–205°). *1,1,3,3,7,7,9,9-Octamethyl-5,10,11-trithiadispiro[3.1.3.2]undecane-2,8-*

dione (**6b**). Yield: 30 mg (17%). Colorless crystals. M. p. 98–101° (MeOH/CH_2Cl_2) ([30]: 100–102°). *2",2",4",4"-Tetramethyldispiro[adamantane-2,2'-[1,2,4]trithiolane-5',3"-cyclobutane]-1"-one* (**8a**). Yield: 70 mg (40%). Colorless crystals. M.p. 113–115° (hexane/CH_2Cl_2). IR (KBr): 2924*m*, 1787*s* (C=O), 1452*m.* ^{1}H-NMR ($CDCl_3$): 1.42 (*s*, 2 Me); 1.45 (*s*, 2 Me); 1.77–1.97, 2.14–2.35 (2*m*, 14 H). ^{13}C-NMR ($CDCl_3$): 21.3 (4 Me); 25.9, 26.3, 26.6, 39.6 (4 CH); 36.6, 37.6, 37.7 (5 CH_2); 66.4 (2 C_q); 86.3 (C_q); 89.2 (C_q); 219.2 (C=O). CI-MS: 356 (22), 355 (100, $[M+1]^+$), 167 (45). Anal. calc. for $C_{18}H_{26}OS_3$ (354.60): C 60.97, H 7.39, S 27.13; found: C 59.26, H 6.89, S 26.98.

Reaction of **7**, **1b**, and **1e**. *1,1,3,3-Tetramethyl-7,7-diphenyl-5,6,8-trithiaspiro[3.4]-octan-2-one* (**8b**). Yield: 240 mg (62%). Colorless crystals. M.p. 99–100° (EtOH/CH_2Cl_2) ([30]: 101–102°).

Reaction of **7**, **1c**, and **1e**. *2,2-Dichloro-1,1,3,3-tetramethyl-7,7-diphenyl-5,6,8-trithiaspiro[3.4]octane* (**8c**). Yield: 230 mg (52%). Colorless crystals. M.p. 115–118° (MeOH/CH_2Cl_2). IR (KBr): 2981*m*, 1466*m*, 1443*s*, 808*m*, 749*m*, 725*s,* 697*s*. ^{1}H-NMR ($CDCl_3$): 1.49 (*s*, 2 Me); 1.63 (*s*, 2 Me); 7.24–7.66 (*m*, 10 arom. H). ^{13}C-NMR ($CDCl_3$): 25.2 (2 Me); 29.5 (2 Me); 59.9 (2 C_q); 88.2 (C_q); 91.8 (C_q); 99.9 (C_qCl_2); 128.2 (6 arom. CH); 129.4 (4 arom. CH); 141.9 (2 arom. C_q). CI-MS: 441 (5, $M^{+\cdot}$), 231 (23), 200 (15), 199 (100). Anal. calc. for $C_{21}H_{22}Cl_2S_3$ (441.51): C 57.13, H 5.02, S 21.79; found: C 57.11, H 4.93, S 21.71.

REFERENCES

[1] J. Nakayama, A. Ishii, *Adv. Heterocycl. Chem.* **2000**, *77,* 221.

[2] K. Okuma, *Sulfur Rep.* **2002**, *23*, 209; K. Okuma, T. Shigetoni, S. Shibata, K. Shioji, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 187.

[3] R. Huisgen, J. Rapp, *J. Am. Chem. Soc.* **1987**, *109*, 902; R. Huisgen, J. Rapp, *Tetrahedron* **1997**, *53*, 939.

[4] G. Mloston, H. Heimgartner, *Helv. Chim. Acta* **1995**, *78*, 1298.

[5] G. Mloston, J. Romanski, H. Heimgartner, *Pol. J. Chem.* **1996**, *70*, 437.

[6] R. Huisgen, G. Mloston, K. Polborn, F. Palacios-Gambra, *Liebigs Ann./Recueil* **1997**, 187.

[7] W. Adam, R. M. Bargon, G. Mloston, *Eur. J. Org. Chem.* **2003**, 4012.

[8] K.-F. Wai, M. P. Sammes, *J. Chem. Soc., Perkin Trans. 1* **1991**, 183.

[9] A. Holm, N. Harrit, I. Trabjerg, *J. Chem. Soc., Perkin Trans. 1* **1978**, 746.

[10] R. Neidlein, J. Tauber, *Arch. Pharm.* **1971**, *304*, 687.

[11] C. Wentrup, P. Kambouris, *Chem. Rev.* **1991**, *91*, 363; C. Wentrup, R. Flamang, *J. Phys. Org. Chem.* **1998**, *11*, 350.

[12] W. Adam, R. M. Bargon, *Eur. J. Org. Chem.* **2001**, 1959; W. Adam, R. M. Bargon, *Chem. Rev.* **2004**, *104*, 251.

[13] J. Fabian, A. Senning, *Sulfur Rep.* **1998**, *21*, 1.

[14] G. Mloston, J. Romanski, H. P. Reisenauer, G. Maier, *Angew. Chem., Int. Ed.* **2001**, *40*, 393.

[15] G. Maier, H. P. Reisenauer, J. Romanski, H. Petzold, G. Mloston, *Eur. J. Org. Chem.* **2006**, 3721.

[16] B. Ya. Kazakov, I. Ya. Postovskii, *Dokl. Chem. (Engl. Transl.)* **1960**, *134*, 1077.

[17] M. G. Ponzo, G. Evindar, R. A. Batey, *Tetrahedron Lett.* **2002**, *43*, 7601.

[18] H. Oshida, A. Ishii, J. Nakayama, *J. Org. Chem.* **2004**, *69*, 1695.

[19] G. Mloston, R. Depczynski, M. Woznicka, P. Laur, U. Englert, C. Hu, H. Heimgartner, *J. Sulfur Chem.* **2005**, *26*, 111.

[20] S. Scheibye, R. Shabana, S.-O. Lawesson, C. Romming, *Tetrahedron* **1982**, *38*, 993.

[21] G. Mloston, J. Romanski, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1995**, *78*, 1067.

[22] G. Mloston, A. Majchrzak, M. Rutkowska, M. Woznicka, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **2005**, *88*, 2624.

[23] G. Mloston, J. Romanski, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1993**, *76*, 2147.

[24] H. Heimgartner, G. Mloston, J. Romanski, in 'Electronic Encyclopedia of Reagents in Organic Synthesis', Eds. L. Paquette, J. Rigby, D. Crich, P. Wipf, John Wiley & Sons, Chichester, Article RN00504.

[25] H. Heimgartner, G. Mloston, in 'Electronic Encyclopedia of Reagents in Organic Synthesis', Eds. L. Paquette, J. Rigby, D. Crich, P. Wipf, John Wiley & Sons, Chichester, Article RN00429.

[26] P. Metzner, R. Rakotonirina, *Tetrahedron* **1985**, *41*, 1289.

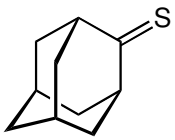
[27] G. Mloston, J. Romanski, A. Swiatek, H. Heimgartner, *Helv. Chim. Acta* **1999**, *82*, 946.

[28] K. Hartke, T. Kissel, J. Quante, R. Matusch, *Chem. Ber.* **1980**, *113*, 1898; C. Len, D. Postel, G. Ronco, P. Villa, C. Goubert, *J. Agric. Food Chem.* **1997**, *45*, 3.

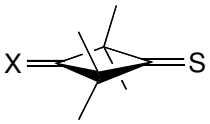
[29] G. Mloston, J. Romanski, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1996**, *79*, 1305.

[30] G. Mloston, G. K. S. Prakash, G. A. Olah, H. Heimgartner, *Helv. Chim. Acta* **2002**, *85*, 1644.

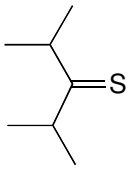
Formulae



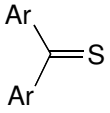
1a

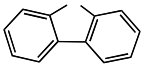


1b X = O
1c X = Cl_2

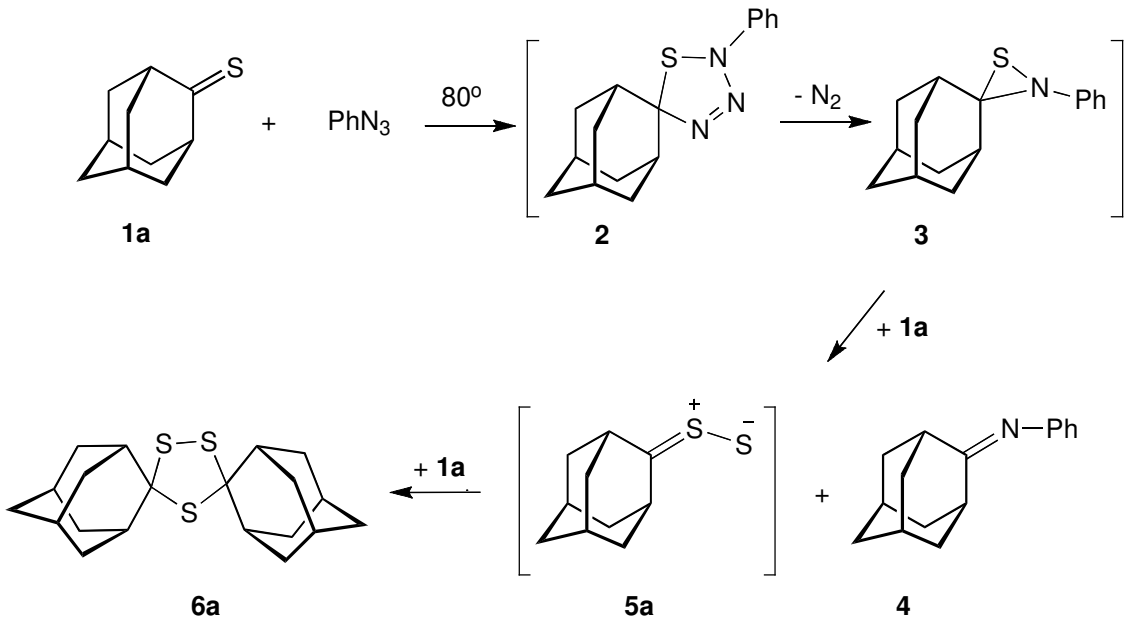


1d

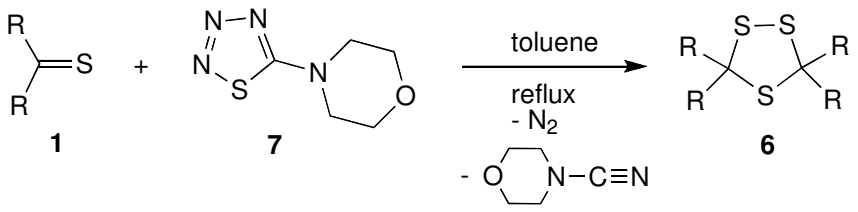


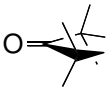
1e Ar = Ph
1f Ar-Ar = 

Scheme 1

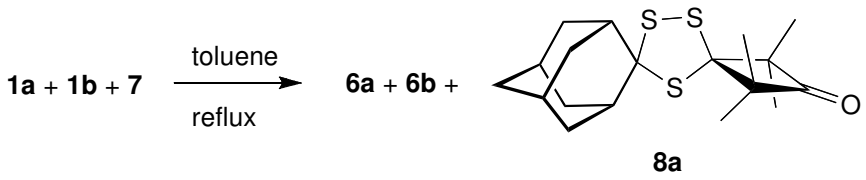


Scheme 2



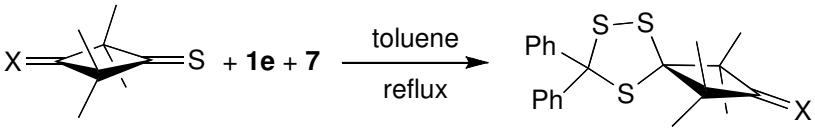
a R-R =  **b** R-R = 

Scheme 3



8a

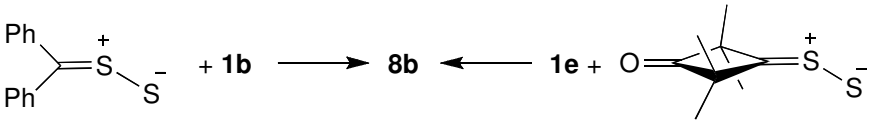
Scheme 4



1b X = O
1c X = Cl_2

8b X = O
8c X = Cl_2

Scheme 5



5f **5b**

Graphical Abstract