dichloromethane was added dropwise under stirring to a mixture of 6.3 g (55 mmol) of **7** and 4.5 g (57 mmol) of pyridine in 20 mL of dry dichloromethane at room temperature. Stirring was continued for 2 h, and the solution was washed successively with water, diluted hydrochloric acid, washed a second time with water, and then dried over calcium chloride. The solvent was removed by distillation and the residue fractionated under reduced pressure. The fraction boiling from 133 to 136 °C at 2×10^{-3} torr consisted of crude **10**. TLC analysis showed the presence of at least five further components; the main impurity was diphenyl disulfide. Further purification was performed by chromatography on silica gel with chloroform as the eluent, yielding **10** as a slightly pale yellow oil: 3.7 g (30%); IR (liquid) 1770 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 90 MHz, FT) δ 1.255, 1.287 (2 s, 6 H, 2 CH_3), 3.540, 3.625, 3.645, 3.729, 3.977, 4.078, 4.183, 4.395, 4.476, 4.496, 4.580 (ABX m, 3 H, CH-CH_2), 7.25-7.48 (m, 5 H, C_6H_5). Anal. Calcd for $C_{12}H_{14}O_2S$ (M_r = 222.3): C, 64.83; H, 6.35. Found: C, 64.79; H, 6.46.

2,2-Dimethyl-3-(phenylsulfonyl)-γ-butyrolactone (3). A large excess of 30% hydrogen peroxide (3.4 g) was added to a solution of 2.8 g (12.6 mmol) of lactone **10** in 65 mL of glacial acetic acid, and the mixture was heated under reflux for 3 h. After the mixture was poured into water, 2.1 g of the crystallized sulfone **3** could be collected by filtration immediately. Extraction of the aqueous phase with dichloromethane and the usual workup yielded a second crop of **3**. Recrystallization from ethyl acetate gave 3.1 g (95%) of **3** as white needles, mp 106 °C, identical with the substance obtained by the oxidation of **1**: IR (KBr) 1145, 1280, 1328 (SO_2), 1790 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 90 MHz, FT) δ 1.421, 1.597 (2 s, 6 H, 2 CH_3), 3.632, 3.716, 3.736, 3.821, 4.114, 4.199, 4.218, 4.303, 4.395, 4.499, 4.606 (ABX m, 3 H, CH-CH_2), 7.54-7.96 (m, 5 H, C_6H_5). Anal. Calcd for $C_{12}H_{14}O_4S$ (M_r = 254.3): C, 56.67; H, 5.55. Found: C, 56.55; H, 5.59.

Registry No. **1**, 10276-07-0; **2**, 10276-08-1; **3**, 87279-52-5; **4**, 97-62-1; **5**, 600-00-0; **6**, 7505-94-4; **7**, 10276-09-2; 7 ethyl ester, 58544-20-0; **10**, 87279-53-6; MeCH=O, 75-07-0; methallyl phenyl sulfone, 49639-05-6; 2,2-dimethyl-3-(phenylsulfonyl)propanenitrile, 87279-54-7; 2,2-dimethyl-3-(phenylsulfonyl)propanoic acid, 38435-02-8.

Synthesis of Thione *S*-Imides by Alkylidenation of Sulfinylanilines and Imination of Sulfines

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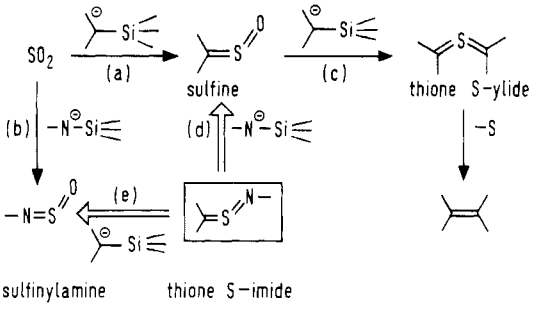
Thione *S*-imides **3** have been synthesized by alkylidenation of sulfinylamines **1** using α-trimethylsilyl carbanions **2**. Imination of sulfines **4** by means of anions of (trimethylsilyl)amines **5** also led to thione *S*-imides **3**. It was found to be essential that in these syntheses the thione *S*-imides are substituted with sterically filled groups.

Alkylidenation of sulfur dioxide by using α-silyl carbanions constitutes a new and convenient route to sulfines[1,2] (thione *S*-oxides; Scheme I, reaction a). Sulfinylamines can be prepared in an analogous manner by imination of sulfur dioxide with anions of silylamines (Scheme I, reaction b).[3] During the synthesis of sulfines by following this modified Peterson reaction, it was found to be essential that the α-silyl carbanion is added to an excess of sulfur dioxide in order to avoid the formation of an olefin as a byproduct;[2,4] e.g., the preparation of fluorenethione *S*-oxide is accompanied by the formation of some bifluorenylidene.[2,4] This side reaction probably involves the reaction of the α-silyl carbanion with already formed sulfine to give a thione *S*-ylide. This heterocumulene is known to be very unstable and loses sulfur readily to give an olefin (Scheme I, reaction c).[2,4] In fact, this alkylidenation of sulfines represents a new entry to thione *S*-ylides.

Extrapolation of these findings leads to the proposal that imination of sulfines with anions of silylamines potentially forms a route to thione *S*-imides. Alternatively, the formation of these thione *S*-imides can be envisaged via alkylidenation of sulfinylamines by means of α-silyl carbanions. Both suggested methods of preparation of thione *S*-imides are incorporated in Scheme I in a retrosynthetic

Scheme I



fashion (reaction d and e, respectively). This paper deals with the results obtained by using both these approaches.

The synthesis of thione *S*-imides has attracted considerable attention in the recent literature. Oae et al.[5] reported for the first time the isolation of these sulfur-centered heterocumulenes. These authors obtained remarkably stable thione *S*-tosylimides by treatment of 1,2-dithiole-3-thiones with chloramine T.[6] As shown by Wentrup et al.,[7] reaction of these thiones with *N*-chlorobenzamide followed by base leads to the corresponding

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(2) van der Leij, M.; Porskamp, P. A. T. W.; Lammerink, B.H.M.; Zwanenburg, B. *Tetrahedron Lett.* **1978**, 811.
(3) Porskamp, P. A. T. W.; Zwanenburg, B. *Synthesis* **1981**, 368.
(4) van der Leij, M. Thesis, University of Nijmegen, 1979.
(5) Tamagaki, S.; Oae, S. *Tetrahedron Lett.* **1972**, 1159. Tamagaki, S.; Sakaki, K.; Oae, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2608; **1974**, *47*, 3084; *Heterocycles* **1974**, *2*, 39.
(6) A modified procedure using tosylamides and bromine was reported by: Koide, A.; Saito, T.; Kawasaki, M.; Motoki, S. *Synthesis* **1981**, 486.
(7) Wentrup, G. J.; Boberg, F. *Justus Liebigs Ann. Chem.* **1978**, 387. Boberg, F.; Puttins, U.; Wentrup, G. J. *Ibid.* **1979**, 689.

0022-3263/83/1948-4582$01.50/0

Scheme II

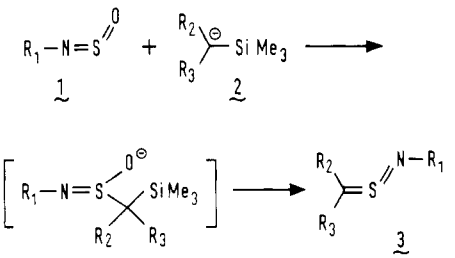
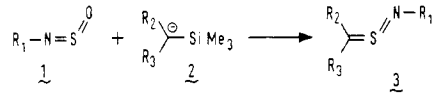
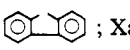


Table I. Thione S-Imides via Alkylidenation of Sulfinylamines



starting materials				product	
no.	R_1	no.	R_2,R_3 [a]	no.	yield, %
1a	2,4,6-(t-Bu)$_3$C$_6$H$_2$	2a	F1	3a	77
1b	2-Me-4,6-(t-Bu)$_2$C$_6$H$_2$	2a	F1	3b	
1c	2,4,6-(t-Bu)$_3$C$_6$H$_2$	2b	Xa	3c	68
1d	4-MeC$_6$H$_4$SO$_2$	2a	F1	3d	

[a] F1 =  ; Xa =  .

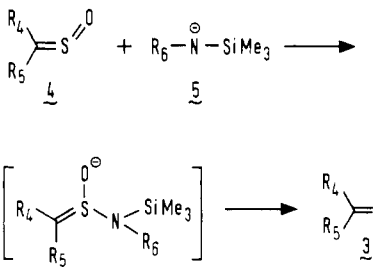
S-benzoylimides. The stability of these 1,2-dithiole-3-thione S-imides was attributed to the presence of the 6-π-electron system in trithiones.[5] In accordance herewith is the fact that Campbell et al.[8] were unable to prepare thione S-imides from aliphatic or aromatic thiones by reactions with chloroamine T. Interestingly, however, stable S-tosylimides can be obtained from dithiobenzoates and chloramine T provided that the substrates are sufficiently sterically hindered.[9] Burgess et al.[10] prepared fluorenethione S-benzoylimide in solution by a 1,3-dehydrohalogenation of an α-chloro sulfenamide. In a similar manner Senning et al.[11] obtained the thermally stable S-tert-butylimides $RSO_2C(SPh)=S=N$-t-Bu. Crossland[12] synthesized an α-oxo thione S-imide using the 1,3-dehydrochlorination method. Reasonably stable fluorenethione S-tosylimides were prepared by Saito and Motoki[13] using a Wittig-type reaction of phosphoniumfluorenylides with N-sulfinyl-p-toluenesulfonamide.

Alkylidenation of Sulfinylanilines

As indicated in Scheme I (reaction e) thione S-imides are the predicted products from the reaction of sulfinyl amines and α-silyl carbanions. From previously prepared thione S-imides it is known that their stability is enhanced by steric congestion.[9] Therefore, sulfinylanilines were selected that had two o-tert-butyl substituents.

Treatment of 2,4,6-tri-tert-butyl-N-sulfinylaniline (**1a**) with the anion of 9-(trimethylsilyl)fluorene (**2a**) indeed resulted in the formation of thione S-imide **3a** in good yield (Scheme II; Table I). Similarly, the anion of 10-(trimethylsilyl)xanthene gave S-imide **3c**. The importance

Scheme III



of steric hindrance was strikingly demonstrated when 2,4-di-tert-butyl-6-methyl-N-sulfinylaniline was subjected to alkylidenation with anion **2a**. We were unable to isolate the desired thione S-imide. Attempts were also made to introduce steric crowding around the anionic carbon atom. However, the methine proton in 2,4,6-$Me_3C_6H_2CH$-(SPh)$SiMe_3$ is sterically shielded to such an extent that strong bases like n-BuLi, NaH, and t-BuLi are unable to accomplish its abstraction. It should be noted that the thione S-imide **3f** which is the predicted product from the expected anion and the sulfinylamine **1b** enjoys sufficient stability for isolation (vide infra). Reaction of N-sulfinyl-p-toluenesulfonamide with anion **2a** does not yield thione S-imide **3d** [p-toluenesulfonamide and 9-(trimethylsilyl)fluorene were obtained in high yield]. It is remarkable that this Peterson alkylidenation of this sulfinylamide is unsuccessful whereas the analogous Wittig olefination leads to the expected thione S-imide, as was shown by Saito et al.[13]

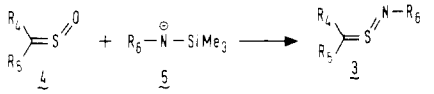
Imination of Sulfines

As outlined in the introduction, an alternative approach to thione S-imides consists of imination of sulfines. To ensure sufficient stability of the products, we selected sterically hindered sulfines and amine components. The anion of N-(trimethylsilyl)-2,4,6-trimethylaniline, **5a** smoothly reacted with sulfine **4a** to give the predicted S-imide **3e** (Scheme III, Table II). The same sulfine was also treated with a series of other sterically hindered amine anions (**5b–e**). In a similar fashion five other sulfines (**4b–f**) were converted into thione S-imides upon reaction with a selection of the above mentioned amine anions. The thione S-imides obtained are compiled in Table II. It was found that an increase of steric crowding gave rise to an increased reaction time and a decreased yield. In order to shorten the reaction time we employed an excess of amine anion. The experimental conditions for tert-butylamine as the amine component needed to be modified to enable the isolation of the rather unstable products **3i** and **3l**. After the reaction of amine anion **5e** with sulfines **4a** and **4b** was completed, 1 equiv of trimethylsilyl chloride was added to convert Me_3SiOLi into volatile hexamethyldisiloxane and LiCl (this is practically insoluble in ether and thus can be removed by filtration; THF cannot be used as the solvent because LiCl dissolves partially). The amine anion **5c** does react with fluorenylidenesulfine **4g**; however, the expected S-imide **3u** is probably too unstable to allow its isolation. From the results of Table II it follows that this imination route can be used for the preparation of a variety of thione S-imides provided that the condition of sufficient steric hindrance is fulfilled.

Thione S-imides can be considered as derivatives of sulfur dioxide and therefore their structure is predicted to be nonlinear.[9] As a consequence, geometrical isomers may be expected for thione S-imides bearing unequal substituents at the carbon atom. The existence of stable E and Z isomers was demonstrated previously for the

(8) Campbell, M. M.; Evgenios, D. M. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2866.
(9) Tangerman, A.; Zwanenburg, B. *Tetrahedron Lett.* **1977**, 259; *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 127.
(10) Burgess, E. M.; Penton, H. R., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 279; *J. Org. Chem.* **1974**, *39*, 2885.
(11) Holm, S.; Boerma, J. A.; Nilsson, N. H.; Senning, A. *Chem. Ber.* **1976**, *109*, 1069.
(12) Crossland, I. *Acta Chem. Scand., Ser. B* **1977**, *B31*, 890.
(13) Saito, T.; Motoki, S. *J. Org. Chem.* **1977**, *42*, 3922.

Table II. Thione *S*-Imides via Imination of Sulfines



starting materials							product			
								yield, %		
no.	R_4[e]	R_5[e]	no.	R_6[e]	equiv[a]	rt,[b] h	no.	oil[c]	crystals[d]	mp, °C
4a	Ar^1	PhS	5a	Ar^1	1.7	1	3e	95	82	99-100.5
4a	Ar^1	PhS	5b	Ar^2	1.2	20	3f	16.5	13	113-115
4a	Ar^1	PhS	5c	Ar^3	1.2	4	3g	80	65	81.5-83
4a	Ar^1	PhS	5d	Ar^4	2.5	1	3h	85	53	104.5-106
4a	Ar^1	PhS	5e	*t*-Bu	1	2	3i	90	43	89-92
4b	Ar^5	PhS	5b	Ar^2	2.3	20	3j	21		
4b	Ar^5	PhS	5c	Ar^3	1.2	20	3k	71	24	133-134
4b	Ar^5	PhS	5e	*t*-Bu	1	2	3l	90		
4c	Ar^5	Ar^1S	5a	Ar^1	2.5	2	3m	85		
4c	Ar^5	Ar^1S	5c	Ar^3	1.2	60	3n	14.6		
4c	Ar^5	Ar^1S	5d	Ar^4	2.3	4	3o	61		
4d	Ar^1	Ar^1S	5a	Ar^1	1.5	20	3p	90	64	119-121
4e	Ar^1	Ph	5a	Ar^1	1.5	20	3q	75	52	115-116.5
4e	Ar^1	Ph	5c	Ar^3	1.5	20	3r	45	30	126-127
4e	Ar^1	Ph	5d	Ar^4	1.2	20	3s	61	40	96-97
4f	Ar^5	(2-Naph)S	5c	Ar^3	4	20	3t	71	40	129.5-131
4g		F1	5c	Ar^3	4	20	3u			

[a] Equivalents of amine. [b] Reaction time. [c] Isolated as an oil. [d] Crystals obtained from the initially isolated oil. [e] Ar^1 = 2,4,6-$(Me)_3C_6H_2$; Ar^2 = 2-Me-4,6-$(t\text{-Bu})_2C_6H_2$; Ar^3 = 2,6-$(i\text{-Pr})_2C_6H_3$; Ar^4 = 2,6-$(Me)_2C_6H_3$; Ar^5 = 2,6-$(Me)_2$-3-$(i\text{-Pr})$-4-$(OMe)C_6H$; F1 =  .

thione *S*-tosylimides derived from 2,4,6-trimethyldithiobenzoates.[9] For the compounds **3e–l** only one isomer was isolated as is indicated by their ^1H NMR spectra. However, the geometrical configuration (*E* or *Z*) could not be established by means of ASIS experiments or NMR shift reagents due to the lack of the other isomer. For the products **3m–o** a mixture of both isomers was obtained. Attempts to separate these isomers, either by chromatography or by crystallization, failed, probably because of an easy interconversion at room temperature. The compounds **3q–s** were isolated as a mixture of isomers after chromatography; however, on being allowed to stand, one of the isomers crystallized. Product **3r** was assigned the *E* geometry on the basis of the low-field absorption of the ortho protons of the phenyl ring resulting from the anisotropic deshielding effect of the S=NR moiety in the syn position. For the crystallized isomers of **3q,s** no deshielding effect was observed for the ortho protons of the phenyl ring, implying that these isomers possess the *Z* geometry.

The thione *S*-imides **3** all show considerable steric crowding. As a consequence thereof they are chemically not very reactive. Attempts to accomplish reactions with 2,3-dimethyl-1,3-butadiene and cyclopentadiene, reagents that do react with less hindered substrates,[10,13] in all cases gave recovery of unchanged thione *S*-imides.

Deimination of compounds **3e,g,p** was achieved by treatment with either 0.5 equiv of phosphorus pentasulfide or 1 equiv of thiophosphoryl bromide in dichloromethane. This reaction closely resembles the deoxygenation of sulfines by these reagents.[14] Therefore, it is suggested that thiosulfines (>C=S=S) are also intermediates in the deimination process.

Experimental Section

Melting points were determined on a Reichert hot-stage microscope and are uncorrected. ^1H NMR spectra were recorded on a Varian E-390 spectrometer with Me_4Si as an internal standard. IR spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer. Mass spectra were obtained with a Varian MAT SM_2B mass spectrometer. Elemental analyses were performed by J. Diersmann (Micro Analytical Department of our University). UV spectra were recorded on a Perkin-Elmer 555 spectrophotometer. THF and diethyl ether were distilled twice over CaH_2. The starting sulfines[1], (trimethylsilyl)amines,[3] and sulfinylamines[3] were prepared as described in the literature. All reaction were carried out under nitrogen. The *n*-BuLi used was a stock solution of 1.6 M in hexane.

Fluorenethione *S*-(2,4,6-Tri-*tert*-butylphenyl)imide (3a). To a solution of 9-(trimethylsilyl)fluorene (5 mmol) in THF (40 mL) was added 1.10 equiv of *n*-BuLi at −78 °C. After being stirred for 1 h at room temperature, the thus-obtained solution was added to a solution of sulfinylamine **1a** (5 mmol) in THF (30 mL) at −78 °C. After being stirred for 1 h at room temperature, the reaction mixture was poured into a saturated aqueous solution of ammonium chloride. The organic layer was dried ($MgSO_4$) and then concentrated. The remaining dark red oil crystallized on standing. Analytically pure product **3a** was obtained by careful washing with diisopropyl ether: mp 141–143 °C; IR (KBr) 954 cm^{-1} (C=S=N); ^1H NMR ($CDCl_3$) δ 1.37 (s, 9 H, *p*-C_4H_9), 1.46 (s, 18 H, *o*-C_4H_9), 7.10–7.80 (m, 9 H, arom), 8.90–9.05 (m, 1 H, arom); UV (CH_3OH) λ_{max} 430 nm (log ε 4.36); mass spectrum, *m/e* 455 (M^+). Anal. Calcd for $C_{31}H_{37}SN$: C, 81.71; H, 8.18; N, 3.07. Found: C, 81.54; H, 8.21; N, 3.06.

Xanthenethione *S*-(2,4,6-Tri-*tert*-butylphenyl)imide (3c). This compound was prepared by following the procedure described for **3a** and starting from 10-(trimethylsilyl)xanthene (5 mmol): mp 108–110 °C; IR (KBr) 920, 932 cm^{-1} (C=S=N); ^1H NMR ($CDCl_3$) δ 1.37 (s, 9 H, *p*-C_4H_9), 1.47 (s, 18 H, *o*-C_4H_9), 6.80–7.50 (m, 9 H, arom), 9.90–10.10 (m, 1 H, arom); UV (CH_3OH) λ_{max} 470 nm (log ε 4.14); mass spectrum, *m/e* 439 (M^+ − S). Anal. Calcd for $C_{31}H_{37}SNO$: C, 78.93; H, 7.91; N, 2.97. Found: C, 78.89; H, 8.10; N, 2.84.

General Procedure for Thione *S*-Imides 3e–h,j,k,m–t. To a solution of *N*-(trimethylsilyl)aniline (for amounts see Table II) in THF (30 mL) was added a 10% excess of *n*-BuLi at 0 °C. After being stirred for 1 h at room temperature, the resulting solution was gradually siphoned into a solution of sulfine **4** (3 mmol) in THF (30 mL) at −78 °C. After the reaction mixture was stirred at room temperature for the period indicated in Table II, the solvents were removed in vacuo. The resulting crude product was

(14) Kuipers, J. A. M.; Lammerink, B. H. M.; Still, I. W. J.; Zwanenburg, B. *Synthesis* **1981**, 295.

purified by chromatography (silica gel, diisopropyl ether/hexane). The thione *S*-imides were obtained as red oils, and some of them crystallized on standing at 0 °C. The crystals were carefully washed with dry hexane, yielding analytically pure products.

All the thione *S*-imides synthesized showed typical infrared C=S=N absorptions between 900 and 1000 cm^{-1} and UV absorptions with λ_{max} between 380 and 400 nm ($\log \epsilon \approx 4$). The ^1H NMR signals were all in full accord with the presented structure.

Alternative Procedure (Nonaqueous Workup). Phenyl 2,4,6-Trimethyldithiobenzoate *thiono*-*S*-*tert*-Butylimide (3i). To a solution of *N*-(trimethylsilyl)-*tert*-butylamine (3.0 mmol) in diethyl ether (50 mL) was added at 0 °C *n*-BuLi (1.10 equiv). After the mixture was stirred for 1 h at room temperature, a solution of sulfine **4a** (3.0 mmol) in diethyl ether (10 mL) was added at −78 °C. Then, after the mixture was stirred another hour, trimethylsilyl chloride (3.3 mmol) was added at room temperature. The precipitated lithium chloride was filtered off, and the filtrate was concentrated in vacuo, affording thione *S*-imide **3i** as a yellow oil which crystallized on standing. Washing with hexane gave pure material: IR (KBr) 992 cm^{-1} (C=S=N); ^1H NMR ($CDCl_3$) δ 1.42 (s, 9 H, *t*-C_4H_9), 2.12 (s, 3H, *p*-CH_3), 2.20 (s, 6 H, *o*-CH_3), 6.53 (s, 2 H, *m*-H), 6.90–7.40 (m, 5 H, arom); UV (CH_3OH) λ_{max} 381 nm ($\log \epsilon$ 3.93); mass spectrum, *m/e* 343 (M^+). Due to instability satisfactory elemental analyses were not obtained.

Phenyl 4-Methoxy-2,6-dimethyl-3-isopropyldithiobenzoate *thiono*-*S*-*tert*-Butylimide (31). This compound was prepared as described for **3i** by starting from sulfine **4b**: IR (NaCl) 990 cm^{-1} (C=S=N); ^1H NMR ($CDCl_3$) δ 1.08, 1.17 [d, 6 H, J = 7.5 Hz, $CH(CH_3)_2$], 1.39 (s, 9 H, *t*-C_4H_9), 2.10, 2.18 (s, 6 H, *o*-CH_3), 2.70–3.30 [m, 1 H, $CH(CH_3)_2$], 3.58 (s, 3 H, OCH_3), 6.30 (s, 1 H, *m*-H), 6.90–7.20 (m, 5 H, arom); UV (CH_3OH) λ_{max} 380 nm. Due to instability satisfactory elemental analyses were not obtained.

Acknowledgment. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. **1a**, 68761-21-7; **1b**, 71740-69-7; **1d**, 4104-47-6; **2a**, 85535-32-6; **2b**, 87463-60-3; **3a**, 87463-61-4; **3b**, 87463-62-5; **3c**, 87463-63-6; **3d**, 63609-88-1; **3e**, 87463-64-7; **3f**, 87463-65-8; **3g**, 87481-60-5; **3h**, 87463-66-9; **3i**, 87463-67-0; **3j**, 87463-68-1; **3k**, 87463-69-2; **3l**, 87481-61-6; (*E*,*E*)-**3m**, 87463-70-5; (*E*,*Z*)-**3m**, 87463-71-6; (*E*,*E*)-**3n**, 87463-72-7; (*E*,*Z*)-**3n**, 87463-73-8; (*E*,*E*)-**3o**, 87463-74-9; (*E*,*Z*)-**3o**, 87463-75-0; **3p**, 87463-76-1; (*E*,*Z*)-**3q**, 87463-77-2; (*E*,*E*)-**3r**, 87463-78-3; (*E*,*Z*)-**3s**, 87463-79-4; **3t**, 87463-80-7; **3u**, 87463-81-8; **4a**, 87463-82-9; **4b**, 87463-83-0; **4c**, 87463-84-1; **4d**, 78610-73-8; **4e**, 78594-05-5; **4f**, 87463-85-2; **4g**, 4440-32-8; **5a**, 87463-86-3; **5b**, 87463-87-4; **5c**, 87463-88-5; **5d**, 87463-89-6; **5e**, 87463-90-9.

Supplementary Material Available: The spectroscopic data for compounds **3e–h,j,k,m–t**. (4 pages). Ordering information is given on any current masthead page.

Palladium-Catalyzed Polyhetero-Claisen Rearrangement of 3-(Allylthio)-1,2,4-triazin-5(4*H*)-ones

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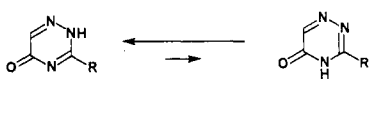
The S → N allylic transposition of 3-(allylthio)-1,2,4-triazin-5(2*H*)-ones (**2**) has been performed successfully by catalysis of a palladium(II) salt, where regioselectivities of the rearrangement (N-2 vs. N-4) are highly dependent on the substitution pattern of the allylic moiety. The rearranged products (**3** and **4**) are converted to 6,7-dihydro-4*H*-thiazolo[2,3-*c*][1,2,4]triazin-4-ones (**10**) and 2,3-dihydro-7*H*-thiazolo[3,2-*b*][1,2,4]triazin-7-ones (**11**), respectively, in high yields by treatment with concentrated sulfuric acid in refluxing formic acid.

Despite the synthetic utility of S → N allylic rearrangement (a general structural transformation: N=CS-CC=C → S=CNCC=C) this rearrangement is one of the least studied polyhetero-Claisen rearrangement,[1] perhaps because the higher temperatures required can lead to side reactions (e.g., double-bond migration of allylic moiety to vinyl sulfides, deallylation, etc.). Furthermore there are no structure–reactivity correlations to permit general use of this rearrangement. For example, 2-(allylthio)benzimidazoles,[2] 2-(allylthio)benzthiazoles,[3] and 2-(allylthio)-imidazolines[4] undergo the S → N allylic rearrangement, while 5-(allylthio)pyrimidines[5] and 8-(allylthio)caffeines[2] are reported not to give the rearranged products.

Scheme I



1,2,4-Triazin-5-ones are of interest in view of their biological activities (for example, metribuzin[6] is a potent herbicide). In this paper we describe the S → N allylic rearrangement of 3-(allylthio)-1,2,4-triazin-5(2*H*)-ones **2**.

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