An Efficient, One-Pot Synthesis of 1,3-Thiazines and 1,2,3,5-Thiatriazines from *N*-(Trimethylsilyl)imines via [4 + 2] Cycloaddition of 1-Thia-3-azadienes

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Dedicated to Professor Manfred Regitz on the occasion of his 60th birthday

The [4 + 2] cycloaddition reaction of 2-amino-1-thia-3-azabutadienes **2**, formed in situ from *N*-(trimethylsilyl)imines **1** and phenyl isothiocyanate, towards electron-poor dienophiles is described. The process is applied to a number of carbo- and heterodienophiles, allowing the regioselective formation of the cycloadducts **3**–**7** with complete *endo*-stereoselectivity.

Since its discovery the Diels–Alder reaction has become one of the most important methods for the preparation of six-membered rings in synthetic organic chemistry.[1] In this reaction two bonds and up to four new stereogenic centers are created in a regio- and stereoselective manner, the selectivity being in general predictable. The synthetic value of this reaction increases to a large extent if one realizes the great number of building blocks (dienes and dienophiles) available.[2] The hetero-Diels–Alder reaction involving heterodienophiles[3] and/or heterodienes[4] has become a powerful tool for the construction of heterocyclic rings, particularly in natural product synthesis.[5] Among heterodienes, 1-azadienes[6] and 2-azadienes[6c,7] have proved to be very useful as precursors of pyridine derivatives. Although cycloadditions involving dienes with two heteroatoms are much less known, examples have been reported mainly for diazadienes[8] as well as for 1-oxa-3-azadienes (*N*-acylimines);[9] reports concerning the thiaazadiene analogs are restricted to 4-bis(trifluoromethyl)-[10] and 4-amino-1-thia-3-azabutadiene derivatives.[11] We have reported a facile preparation of substituted 2-amino-1-thia-3-azadienes **2** from *N*-(trimethylsilyl)imines **1**[12] and their ability to undergo intermolecular[13] and intramolecular[14] [4 + 2] cycloaddition reactions (Figure 1). We disclose herein our results on the [4 + 2] cycloaddition of 1-thia-3-azadienes **2** towards a number of electron-poor alkenes and alkynes as well as azo dienophiles leading to 1,3-thiazine and 1,2,3,5-thiatriazine derivatives.[15]

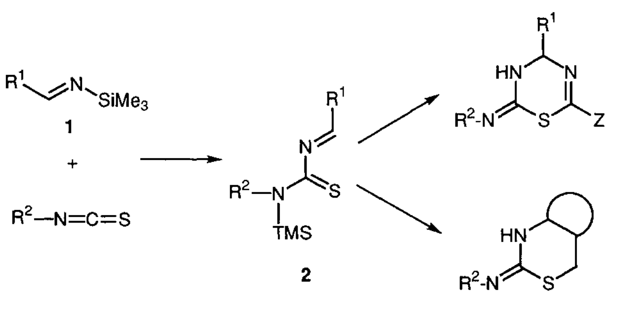


Figure 1

Although the preparation of the starting 1-thia-3-azabutadienes **2** can be quantitatively accomplished by treatment of *N*-(trimethylsilyl)imines **1** with phenyl isothiocyanate at 60 °C in toluene,[12] compounds **2** need not be isolated. Therefore, throughout this work, heterodienes **2** are simply formed in situ and reacted with the appropriate dienophile in the same solvent and under the specific reaction conditions (see Experimental and Table 1).

Dimethyl acetylenedicarboxylate (DMAD) ($R^2 = CO_2Me$; Scheme 1) was first chosen as a suitable dienophile and we found that its reaction with heterodienes **2** was complete after stirring for 10 hours in toluene at 60 °C. Aqueous workup of the resulting mixture gave almost quantitatively substituted 3,4-dihydro-1,3-thiazines **3a, b** as yellow oils, which were purified by column chromatography (Table 1). Compounds **3a, b** were characterized on the basis of microanalytical, spectroscopic (IR, ^1H, and ^{13}C NMR), and mass spectrometric data (Table 2); they exist in solution as the *exo* imino tautomers according to previous studies.[14] Evidence for the complete regioselectivity of the reaction was obtained when methyl propiolate was used and single cycloadducts **3c–e** were cleanly formed, the other regioisomers not being detected in the crude reaction mixture (Scheme 1; Tables 1, 2). The regiochemistry shown was readily deduced from the ^1H NMR spectra, thus, the H_4 and H_6 ring hydrogens appear as two singlets in the ranges $\delta = 5.8–6.2$ and 7.7–7.8, respectively, in accordance with the resonance of H_4 in **3a, b** ($\delta = 5.7–5.8$).

Table 1. 1,3-Thiazine **3–5**, 1,2,3,5-Thiatriazine **6**, **7** and Triazole **8** Rings Prepared

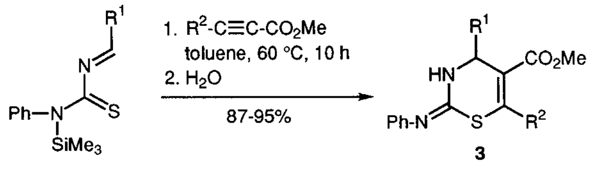
Product[a]	Reaction Conditions[b] *T*(°C)/*t*(h)	Yield[c] (%)	mp[d] (°C)
3a	60/10	92	oil
3b	60/10	87	oil
3c	60/10	88	178–179
3d	60/10	95	130–131
3e	60/10	92	146–147
4a	60/10	80	160–161
4b	60/10	78	163–164
4c	60/10	80	120–121
5	60/10	78	207–208
6a	25/6	90	145–146
6b	25/6	88	127–128
6c	25/6	85	134–135
7	25/6	81	131–132
8	130/18	50	oil

[a] Satisfactory microanalyses obtained: C ± 0.27, H ± 0.16, N ± 0.18.

[b] All the reactions were carried out in toluene under an inert atmosphere of nitrogen.

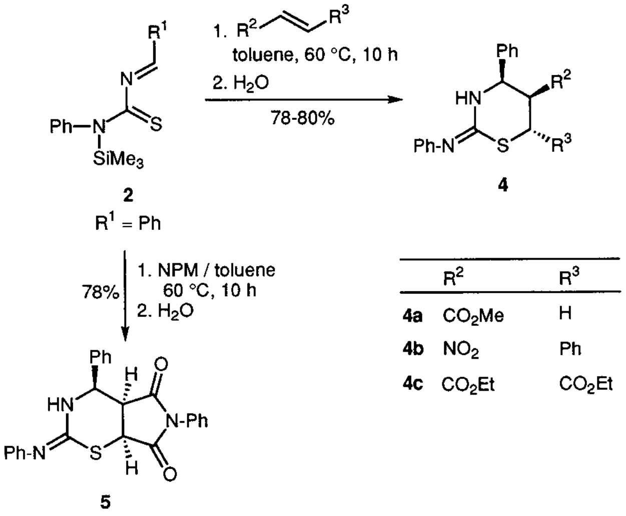
[c] Yields refer to isolated products. Overall yields of **3–7** based on *N*-(trimethylsilyl)imines **1**; yield of compound **8** from **6a**.

[d] Recrystallized from hexane/$CHCl_3$. Mp were measured in open capillary tubes using a Buchi-Tottoli apparatus and are uncorrected.



3	R^1	R^2
a	Ph	CO_2Me
b	2-Thienyl	CO_2Me
c	Ph	H
d	2-Thienyl	H
e	$4\text{-}MeOC_6H_4$	H

Scheme 1



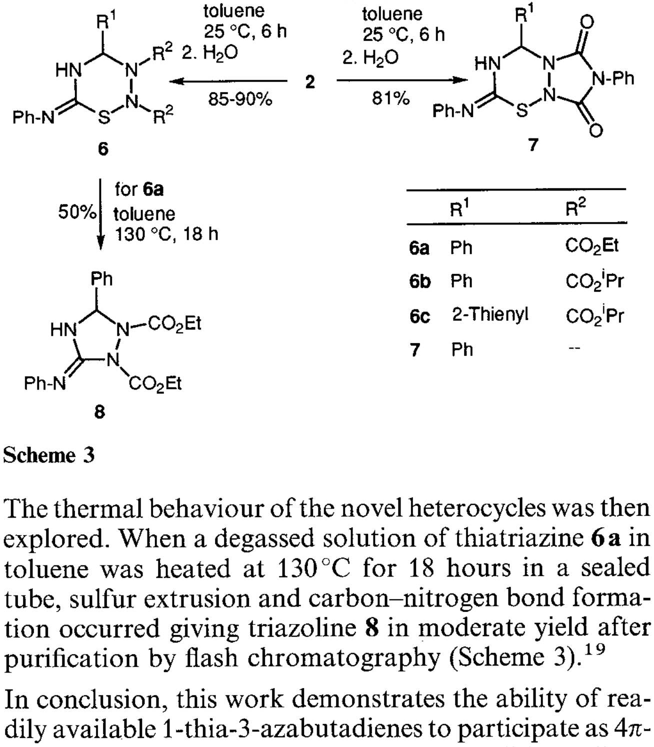
	R^2	R^3
4a	CO_2Me	H
4b	NO_2	Ph
4c	CO_2Et	CO_2Et

Scheme 2

Then, the reactivity of **2** towards alkenes having electron-withdrawing substituents was tested and the stereoselectivity studied (Scheme 2; Tables 1, 2). Thus, treatment of heterodiene **2** ($R^1 = Ph$) with methyl acrylate ($R^2 = CO_2Me$; $R^3 = H$) under the above reaction conditions resulted in the formation of a very clean reaction mixture whose ^1H NMR revealed the presence of the *endo* cycloadduct **4a** as the sole regio- and stereoisomer, which was washed with hexane and recrystallized from hexane–chloroform. The ^1H NMR resonance of H_4 at $\delta = 5.3$ as a doublet with $J = 3.6$ Hz is in agreement with structure **4a** and rules out other isomers. We also found that heterodiene **2** ($R^1 = Ph$) cycloadded to (*E*)-β-nitrostyrene ($R^2 = NO_2$; $R^3 = Ph$) (toluene, 60 °C, 10 h) to yield only the single *endo* cycloadduct **4b** with a *cis* relationship between the C_4 and C_5 substituents; thus, the coupling constants obtained in the ^1H NMR spectra ($J = 4.4$ and 9.1 Hz for H_4-H_5 and H_5-H_6, respectively) reflect a *cis, trans* arrangement for H_4, H_5, H_6. Diethyl fumarate was also able to undergo [4 + 2] cycloaddition at 60 °C to yield exclusively the cycloadduct **4c** arising again from an *endo* transition state; thus, the ring hydrogen atoms of the cycloadduct resonate at $\delta = 3.5$ (dd, $J = 9.8$ and 3.9 Hz, H_5), 4.2 (d, $J = 9.8$ Hz, H_6) and 5.3 (d, $J = 3.9$ Hz, H_4). When diethyl maleate was stirred with heterodiene **2** ($R^1 = Ph$) at 60 °C, no reaction took place at all; however, raising the reaction temperature to 100 °C and stirring the mixture for 18 hours led to the formation of the same thiazine **4c** (65 % yield) as in the case of diethyl fumarate, probably as a consequence of maleate-to-fumarate isomerization.[16] However, we observed that the treatment of the heterodiene **2** ($R^1 = Ph$) with the *cis* dienophile, *N*-phenylmaleimide (NPM), which can be regarded as a masked maleate diester, resulted in the stereoselective formation of the *cis*-fused cycloadduct **5** as the sole observable reaction product.

The above cycloaddition reactions show that 1,3-thiazine derivatives are easily made in one pot and with high yield from trimethylsilyl imines, phenyl isothiocyanate and electron-poor alkenes or alkynes. The importance of this heterocyclic nucleus is well recognized and its chemistry and applications have been reviewed by Quiniou and Guilloton.[17]

At this point, we turned our attention to the use of heterodienophiles, particularly azo derivatives, since the expected cycloadducts would contain the 1,2,3,5-thiatriazine skeleton, which has not been described in the literature as far as we are aware[18] (Scheme 3; Tables 1, 2). Accordingly, we found that stirring at room temperature for 6 hours of an equimolecular mixture of thiaazadienes **2** and dialkyl azodicarboxylates in toluene followed by aqueous workup resulted in the formation of a solid reaction mixture, which was washed with hexane to give the corresponding thiatriazines **6a–c** in excellent yields and high purity. Furthermore, cyclic azo derivatives also underwent smooth cycloaddition at room temperature; thus, fused thiatriazine **7** was isolated as the sole product from the reaction of **2** ($R^1 = Ph$) and *N*-phenyltriazolinedione (PTDA) under the above reaction conditions.



	R^1	R^2
6a	Ph	CO_2Et
6b	Ph	$CO_2{}^iPr$
6c	2-Thienyl	$CO_2{}^iPr$
7	Ph	--

Scheme 3

The thermal behaviour of the novel heterocycles was then explored. When a degassed solution of thiatriazine **6a** in toluene was heated at 130 °C for 18 hours in a sealed tube, sulfur extrusion and carbon–nitrogen bond formation occurred giving triazoline **8** in moderate yield after purification by flash chromatography (Scheme 3).[19]

In conclusion, this work demonstrates the ability of readily available 1-thia-3-azabutadienes to participate as 4π-components in hetero-Diels–Alder cycloadditions allowing regio- and stereoselective preparation of a wide range

Table 2. Spectral Data of Compounds **3**–**8**

Product	IR (Nujol)[a] ν (cm^{-1})	^{1}H NMR (300 MHz, $CDCl_3$/TMS)[b] δ, J (Hz)	^{13}C NMR (75 MHz, $CDCl_3$/TMS)[b] δ	MS[c] M$^+$ (%)
3a	3300, 1690, 1670	3.7 (s, 3H), 3.8 (s, 3H), 5.7 (s, 1H), 7.0–7.5 (m, 11H)	165.3 (s), 163.2 (s), 147.8 (s), 140.8 (s), 138.5 (s), 133.2 (s), 130.5 (s), 128.6 (d), 128.2 (d), 127.6 (d), 127.1 (d), 123.2 (d), 120.0 (d), 62.1 (d), 53.0 (q), 52.3 (q)	382 (15)
3b	3310, 1690, 1680	3.7 (s, 3H), 3.8 (s, 3H), 5.8 (s, 1H), 6.8–7.2 (m, 9H)	166.1 (s), 164.2 (s), 149.6 (s), 146.5 (s), 145.1 (s), 142.1 (s), 139.1 (s), 128.7 (d), 128.4 (d), 128.0 (d), 127.9 (d), 123.3 (d), 120.2 (d), 60.1 (d), 52.1 (q), 51.8 (q)	
3c	3200, 1700	3.6 (s, 3H), 5.8 (s, 1H), 7.0–7.4 (m, 11H), 7.7 (s, 1H)	163.7 (s), 148.2 (s), 144.5 (s), 142.0 (s), 138.6 (s), 131.5 (d), 129.1 (d), 128.7 (d), 128.2 (d), 125.0 (d), 123.8 (d), 121.2 (d), 57.3 (d), 52.2 (q)	324 (37)
3d	3300, 1710	3.7 (s, 3H), 6.2 (s, 1H), 6.8 (s br, 1H), 6.9–7.2 (m, 8H), 7.7 (s, 1H)	163.4 (s), 148.0 (s), 144.2 (s), 142.9 (s), 132.1 (d), 128.9 (d), 126.4 (d), 124.8 (s), 124.6 (d), 124.4 (d), 123.7 (d), 121.1 (d), 52.8 (d), 52.1 (q)	330 (42)
3e	3270, 1700	3.7 (s, 3H), 3.8 (s, 3H), 6.2 (s, 1H), 6.8–7.2 (m, 10H), 7.8 (s, 1H)	165.0 (s), 159.5 (s), 147.1 (s), 144.2 (s), 134.7 (s), 129.0 (d), 128.0 (d), 123.6 (d), 121.2 (d), 113.9 (d), 56.6 (d), 55.2 (q), 52.1 (q)	354 (33)
4a	3300, 1720	3.0–3.2 (m, 3H), 3.6 (s, 3H), 5.3 (d, J = 3.6 Hz, 1H), 7.0–7.4 (m, 11H)	171.1 (s), 150.0 (s), 142.6 (s), 139.3 (s), 128.2 (d), 127.7 (d), 127.2 (d), 126.9 (d), 122.9 (d), 121.2 (d), 58.2 (d), 51.8 (q), 42.8 (d), 22.8 (t)	326 (47)
4b	3300, 1680	4.9 (d, J = 9.1 Hz, 1H), 5.41 (d, J = 4.4 Hz, 1H), 5.46 (dd, J = 9.1, 4.4 Hz, 1H), 7.1–7.5 (m, 16H)	149.3 (s), 140.0 (s), 136.6 (s), 135.4 (s), 129.1 (d), 129.0 (d), 128.9 (d), 128.6 (d), 128.3 (d), 127.5 (d), 123.6 (d), 120.7 (d), 88.9 (d), 62.5 (d), 43.1 (d)	389 (25)
4c	3300, 1710	1.1 (t, J = 7.1 Hz, 3H), 1.2 (t, J = 7.1 Hz, 3H), 3.5 (dd, J = 9.8, 3.9 Hz, 1H), 4.0 (m, 2H), 4.1 (q, J = 7.1 Hz, 2H), 4.2 (d, J = 9.8 Hz, 1H), 5.3 (d, J = 3.9 Hz, 1H), 7.0–7.4 (m, 11H)	170.0 (s), 169.3 (s), 148.5 (s), 141.4 (s), 139.1 (s), 128.7 (d), 128.3 (d), 127.7 (d), 127.0 (d), 123.1 (d), 120.9 (d), 62.0 (t), 61.1 (t), 59.0 (d), 45.2 (d), 40.1 (d), 13.8 (q), 13.7 (q)	412 (36)
5	3300, 1680, 1670	4.0 (dd, J = 10, 4 Hz, 1H), 4.5 (d, J = 10 Hz, 1H), 5.0 (d, J = 4 Hz, 1H), 7.1–7.8 (m, 16H)	[d]	413 (9)
6a	3300, 1690	0.8 (t, J = 8 Hz, 3H), 1.3 (t, J = 8 Hz, 3H), 3.8 (m, 2H), 4.3 (q, J = 8 Hz, 2H), 5.6 (s br, 1H), 7.0 (s, 1H), 7.1–7.6 (m, 10H)	154.4 (s), 145.5 (s), 139.1 (s), 138.9 (s), 128.9 (d), 128.0 (d), 127.3 (d), 123.7 (d), 120.7 (d), 69.0 (d), 63.6 (t), 63.3 (t), 14.3 (q), 13.7 (q)	414 (< 1)
6b	3313, 1700	0.7 (d, 3H), 0.8 (d, 3H), 0.9 (d, 3H), 1.0 (d, 3H), 5.2 (m, 1H), 5.4 (m, 1H), 6.9 (s, 1H), 7.0–7.5 (m, 11H)	161.1 (s), 160.2 (s), 153.4 (s), 139.1 (s), 133.2 (s), 129.4 (d), 128.8 (d), 128.1 (d), 127.5 (d), 125.0 (d), 123.2 (d), 71.3 (d), 69.2 (d), 60.8 (d), 18.1 (q), 17.1 (q), 15.2 (q)	442 (< 1)
6c	3300, 1710	0.8 (d, 3H), 0.9 (d, 3H), 1.0 (d, 3H), 1.1 (d, 3H), 5.3 (m, 1H), 5.5 (m, 1H), 6.8 (s, 1H), 7.0–7.8 (m, 9H)	160.1 (s), 159.7 (s), 154.3 (s), 142.0 (s), 132.2 (s), 129.3 (d), 128.9 (d), 127.8 (d), 126.3 (d), 124.6 (d), 122.3 (d), 70.1 (d), 68.2 (d), 63.1 (d), 17.1 (q), 16.5 (q), 15.9 (q), 15.8 (q)	448 (< 1)
7	3300, 1690	6.8 (s, 1H), 7.1–7.6 (m, 16H)	155.1 (s), 152.9 (s), 143.8 (s), 138.4 (s), 137.3 (s), 130.3 (s), 129.2 (d), 129.0 (d), 128.7 (d), 128.5 (d), 126.3 (d), 125.4 (d), 123.6 (d), 118.5 (d), 84.6 (d)	415 (3)
8	3300, 1680	1.4 (m, 6H), 4.4 (m, 4H), 6.8 (s, 1H), 7.1–7.9 (m, 10H), 8.6 (s br, 1H)	158.0 (s), 153.1 (s), 146.5 (s), 139.4 (s), 138.2 (s), 128.9 (d), 128.3 (d), 128.1 (d), 125.9 (d), 122.9 (d), 118.1 (d), 84.3 (d), 63.4 (t), 63.2 (t), 14.2 (q), 14.0 (q)	382 (6)

[a] Recorded on a Philips PU 9716.

[b] Recorded on a Brucker AC-300.

[c] Recorded on a Hewlett-Packard 5987 A spectrometer.

[d] Because of its very low solubility in the common solvents a good quality spectrum of **5** could not be obtained.

of nitrogen- and sulfur-containing heterocycles; moreover, it is remarkable that the reaction takes place in one pot from simple trimethylsilyl imines, with very high yields and under mild reaction conditions. This procedure is applied to the synthesis of a new class of heterocycles by simply using reactive azodicarboxylate acid esters as dienophiles.

IR spectra were recorded on a Philips PU 9716 and NMR spectra were performed on a Bruker AC-300 spectrometer using $CDCl_3$ as solvent and tetramethylsilane as an internal reference. Mass spectra were obtained by EI (70 eV) from a Hewlett-Packard 5987 apparatus. Melting points were measured in open capillary tubes using a Buchi-Tottoli apparatus, and are uncorrected.

All reactions were run under a nitrogen atmosphere. All solvents used were distilled prior to use. *N*-(Trimethylsilyl)imines **1**[20] and 1-thia-3-azabutadienes **2**[12] were prepared according to previous reports. All other reagents were commercially available and were used as received.

Substituted 2-(Phenylimino)-1,2,3,4-tetrahydro-1,3-thiazines, 3, 2-(Phenylimino)hexahydro-1,3-thiazines 4 and 5, and 2-(Phenylimino)hexahydro-1,2,3,5-thiatrizines 6 and 7; General Procedure:

A mixture of *N*-(trimethylsilyl)imine **1**[20] (5.4 mmol) and phenyl isothiocyanate (730 mg, 5.4 mmol) in toluene (30 mL) was stirred at 60 °C overnight. The resulting red solution was cooled, the dienophile (5.4 mmol) added and stirring continued at 25–60 °C for 6–10 h (see Table 1). The mixture was re-cooled, treated with water (25 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The organic layer was dried (Na_2SO_4), filtered and evaporated at reduced pressure. The cycloadducts thus obtained were subjected to flash chromatography (compounds **3a, b**: silica gel; toluene–Et_2O, 10:1) or triturated with hexane and recrystallized from hexane–$CHCl_3$ (compounds **3c–e, 4–7**). Reaction yields and mps are given in Table 1, and spectroscopic and analytical data are collected in Table 2.

Diethyl 5-Phenyl-3-(phenylimino)-4,5-dihydro-3*H*-1,2,4-triazoline-1,2-dicarboxylate (8):
A degassed solution of thiatriazine **6a** (1 mmol) in toluene (10 mL) was heated at 130 °C in a sealed tube. After 18 h, the reaction mixture was cooled and the solvent evaporated at reduced pressure. The resulting crude mixture was subjected to flash chromatography (silica gel; toluene–Et_2O, 10:1) to give pure triazoline **8** as a yellow oil in 50% yield (Tables 1, 2).

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(19) For related sulfur extrusion processes in sulfur–nitrogen containing heterocyclic compounds, see ref. 18, p 1065.

(20) For the preparation of *N*-(trimethylsilyl)imines **1**, see: Hart, D.J.; Kanai, K.-I.; Thomas, D.G.; Yang, T.-K. *J. Org. Chem.* **1983**, *48*, 289.