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CONVENIENT SYNTHESIS OF 2,3-DIHYDRO-1,2,4-THIADIAZOLES, 4,5-DIHYDRO-1,3-THIAZOLES, AND 1,3-THIAZOLES THROUGH A [4+1]-TYPE OXIDATIVE RING CLOSURE OF 1,3-THIAZA-1,3-BUTADIENES

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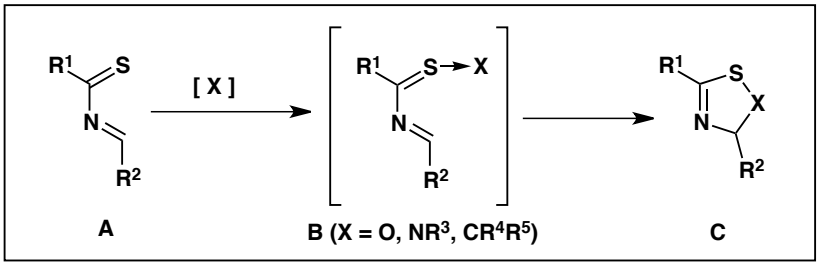
Abstract – 1,3-Thiaza-1,3-butadienes bearing an *N,N*-dimethylamino group at the C-2 position were efficiently converted into 5*H*-1,2,4-oxathiazoles, 2,3-dihydro-1,2,4-thiadiazoles, 4,5-dihydro-1,3-thiazoles, and 1,3-thiazoles through an oxidative ring closure by treating with *m*CPBA, chloramine-T, metal carbenoids, or dichlorocarbene, respectively, *via* the ring closure of *in situ* generated heterocumulene-type reactive species involving thione *S*-oxides, thione *S*-imides, and thiocarbonyl ylides.

INTRODUCTION

Recently, sulfur- and nitrogen-containing five-membered heterocyclic ring systems are widely recognized as important ring systems of a variety of biologically-active natural products[1] such as bacteriocides, fungicides, herbicides, and antibiotics, and numerous preparative methods for these compounds have been reported to date.[2] However, in contrast to the preparation of 3,5-disubstituted 1,2,4-thiadiazole derivatives bearing the same substituents through oxidative dimerization of primary thioamides, syntheses of 1,2,4-thiadiazoles and 1,3-thiazoles bearing different substituents was not simple due to the requirement of regioselectivity in the formal [3+2] coupling, formal [4+1] coupling, or ring closure of some nonsymmetrical precursors in the key steps. The divergent synthetic utility of 1,3-chalcogenaza-1,3-butadienes as the four-atom building blocks of a variety of sulfur- and nitrogen-containing heterocyclic ring systems has been widely recognized along with the progress in the chemistry of 1,3-thiaza-1,3-butadienes during these decades,[3] and, recently, much interest have been focused onto their oxidized variants in the light of their functionalized heterocumulene-like structures and

the potential reactivity as the new versatile building blocks of such five-membered heterocycles. However, in spite of the wide synthetic potentiality of these compounds originated from their characteristic structures bearing the nucleophile-sensitive and electrophile-sensitive moieties in one molecules, only limited studies on the [4+1]-type oxidative ring closure of 1,3-thiaza-1,3-butadienes have been carried out to date.[4]

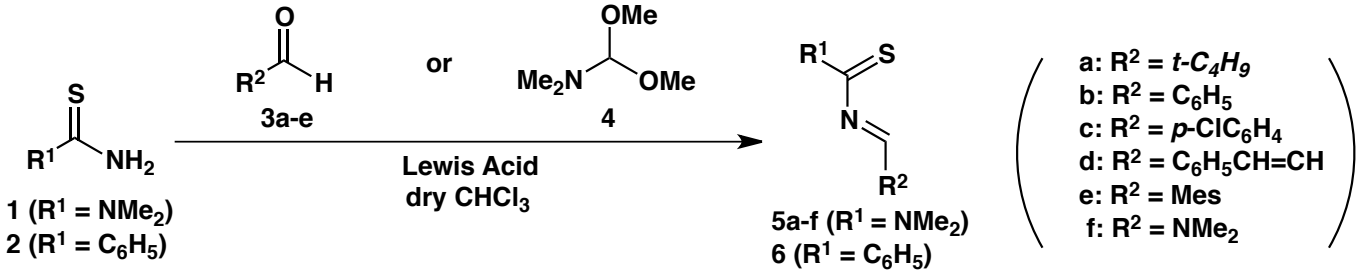
In the course of the studies on chalcogenocarbonyl functionalities connecting with π-conjugation systems, limited studies on the convenient routes for the generation of 1,3-thiaza-1,3-butadienes **A** have been carried out only through thermal cycloreversion of 6*H*-1,3,5-oxathiazines, and we also reported the extension of the methodology to their oxidized variants, such as 1,3-thiaza-1,3-butadiene *S*-oxides and 1,3-thiaza-1,3-butadiene *S*-sulfides, for the synthesis of 5*H*-1,2,4-oxathiazoles and 3*H*-1,2,4-dithiazoles, respectively.[5] These successful results urged us to the *in situ* generation and of other oxidized variants of 1,3-thiaza-1,3-butadienes by using the same methodology in the light of the synthetic utilities of such compounds as the building blocks of a variety of heterocycles. However, 6*H*-1,3,5-oxathiazines were unreactive toward chloramine-T, carbenes, and metal carbenoids in contrast to *m*CPBA, and several attempts for generation of 1,3-thiaza-1,3-butadiene *S*-imides and *S*-ylides through the retro [4+2]-type methodology from 6*H*-1,3,5-oxathiazine derivatives afforded the unsuccessful results in all cases. In order to realize a new synthesis of 2,3-dihydro-1,2,4-thiadiazoles and 5,6-dihydro-1,3-thiazoles by using a similar [4+1]-type protocol to our previous results, we just had an expectation that the use of isolable 1,3-thiaza-1,3-butadienes **A** would enable us to realize the methodology. Our previous findings on the conversion of 6*H*-1,3,5-oxathiazines into 5*H*-1,2,4-oxathiazoles and 3*H*-1,2,4-dithiazoles also supported us to generation and the subsequent ring closure of intermediary oxidized variants **B** from 1,3-thiaza-1,3-butadienes **A** bearing a highly reactive thiocarbonyl functionality as the new precursors of five-membered ring heterocycles **C**. In this paper, we report a preparation of 1,3-thiaza-1,3-butadienes and the subsequent [4+1]-type coupling reactions by the treatment of various oxidizing agents toward the sulfur atom of the heterodienes to form 2,3-dihydro-1,2,4-thiadiazoles, 4,5-dihydro-1,3-thiazoles, and 1,3-thiazoles.



RESULTS AND DISCUSSION

N,N-Dimethylthiourea (**1**, $R^1 = NMe_2$), prepared from *N,N*-dimethylcyanamide and H_2S gas,[6] was treated with pivalaldehyde (**3a**) and BF_3•OEt_2 to afford the corresponding heterodiene **5a** bearing an *N,N*-dimethylamino group at the C-2 position in high yield. Product **5a** was stable enough toward the exposure to air and sunlight, but was unstable toward the contact with silica gel. A similar reaction of **1** with aromatic aldehydes **3b-e** also afforded the corresponding heterodienes **5b-e** in moderate yields, and the use of aliphatic aldehydes, such as 2-methylpropanal and cyclohexanecarbaldehyde, as the substrates, in turn, resulted in the formation of complex mixture. Therefore, it is assumed that the stability of the heterodienes would be affected by the steric bulkiness and/or the aromatic stabilization of substituent R^2. Heterodienes, **5f** ((*N'*-dimethylaminothiocarbamoyl)-*N,N*-dimethylformamidine, $R^1 = R^2 = NMe_2$) and **6** (*N'*-thiobenzoyl-*N,N*-dimethylformamidine, $R^1 = C_6H_5$, $R^2 = NMe_2$), both bearing an *N,N*-dimethylamino group at the C-4 position, were also synthesized by treating compound **1** or thiobenzamide (**2**) with *N,N*-dimethylformamide dimethyl acetal (**4**) according to the reported methods.[7,8] All the results of the reactions of **1** with aldehydes **2a-e** are summarized in Table 1.

Table 1. Preparation of 1,3-Thiaza-1,3-butadienes **5** and **6** bearing an *N,N*-Dimethylamino Group at the C-2 or C-4 Position

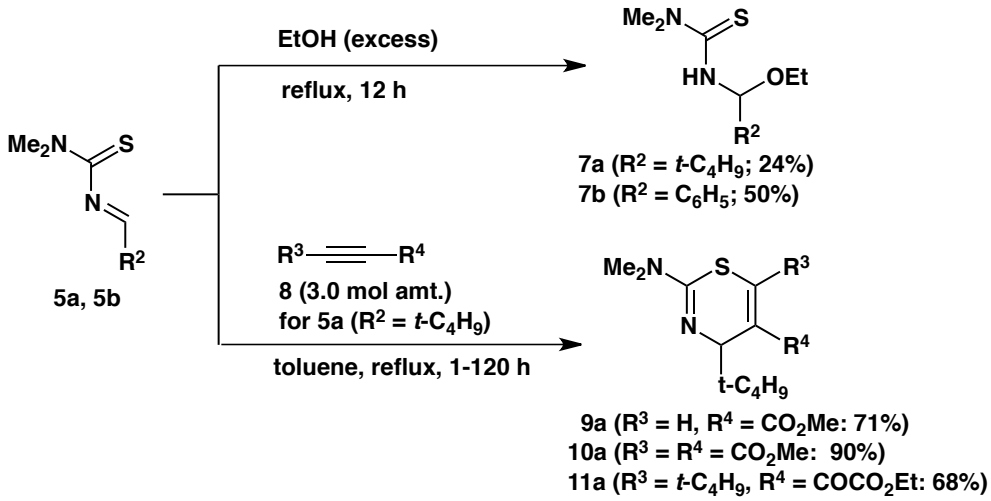


Substrate		Reagent		Lewis Acid	Temp	Time	Product	
R^1	**1** or **2**	R^2	**3** or **4** (mol amt.)	(mol amt.)	/ °C	/ h	Yield / % [a]	**5** or **6**
NMe_2	**1**	*t*-C_4H_9	**3a** (4.0)	BF_3•OEt_2 (3.2)	0	12	93	**5a**
NMe_2	**1**	*t*-C_4H_9	**3a** (4.0)	$SnCl_4$ (2.5)	0	12	complex mixture	
NMe_2	**1**	C_6H_5	**3b** (4.0)	BF_3•OEt_2 (4.0)	0	18	41	**5b**
NMe_2	**1**	*p*-ClC_6H_4	**3c** (2.0)	BF_3•OEt_2 (2.5)	0	18	24	**5c**
NMe_2	**1**	C_6H_5CH=CH	**3d** (2.0)	BF_3•OEt_2 (2.5)	rt	24	14	**5d**
NMe_2	**1**	Mes	**3e** (2.0)	BF_3•OEt_2 (1.8)	0	24	42	**5e**
NMe_2	**1**	NMe_2	**4** (2.5)	-	reflux	2	92	**5f**
C_6H_5	**2**	NMe_2	**4** (2.0)	-	rt	20 min	94	**6**

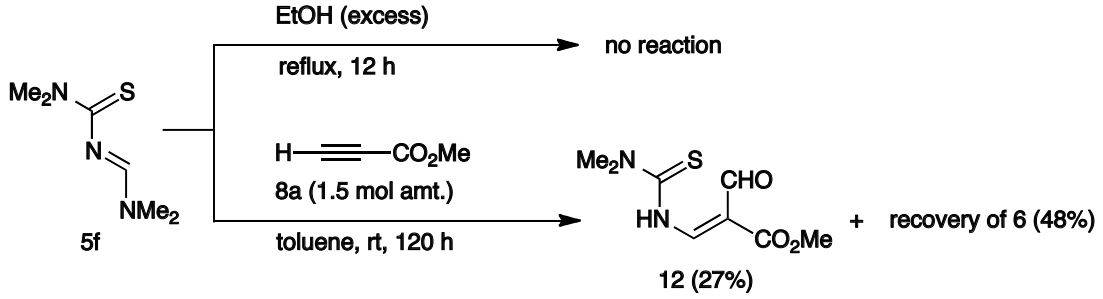
[a]Isolated yields.

Heating of **5a** or **5b** in an ethanolic media afforded the corresponding 1,4-adducts **7a** or **7b**, respectively.[5] In contrast, a similar heating of **5f** or **6** in ethanol only gave the recovery of substrates. These results suggested that the electron-donating *N,N*-dimethylamino group bound to the C-4 position of heterodienes

5f and **6** affects the lowering of the reactivity toward the nucleophilic attack at the C-4 position. Similar heating of a toluene solution of **5a** and dienophiles **8** under refluxing temperature also afforded the corresponding [4+2] cycloadducts **9a**-**11a** in high yields,[3] and these results indicated that heterodienes **5** shows the similar reactivity to that of the previously reported 1,3-thiaza-1,3-butadienes.[5] Interestingly, thermal reaction of **5f** in the presence of methyl propiolate (**8a**) afforded thioenamide **12** in 27 % yield *via* a plausible pathway involving cycloaddition of **5f** and **8a** and the subsequent hydrolytic ring cleavage of the intermediary [4+2] cycloadduct. All results are summarized in Scheme 1 and Scheme 2.



Scheme 1. Reaction of 1,3-Thiaza-1,3-butadienes **5a**, **b** with Ethanol or Acetylenic Dienophiles **8**



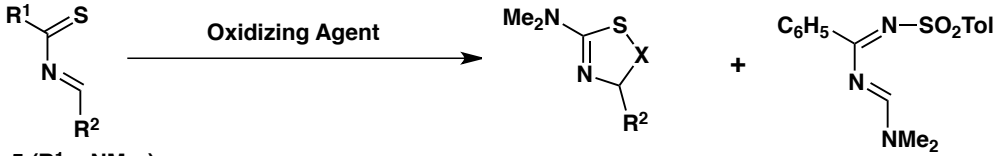
Scheme 2. Reaction of 1,3-Thiaza-1,3-butadiene **5f** with Ethanol or Methyl Propiolate (**8a**)

When a $CHCl_3$ solution of 1,3-thiaza-1,3-butadiene **5a** (R^1 = NMe_2, R^2 = *t*-C_4H_9) was treated with *m*CPBA (1.5 mol amt.) at 0 °C, 5*H*-1,2,4-oxathiazoles **13a** was obtained in moderate yields in a similar manner to our previous cases starting from *m*CPBA oxidation of 6*H*-1,3,5-oxathiazine derivatives. On the other hand, a similar *m*CPBA oxidation of **5b** or **5c** resulted in the formation of complex mixture, and the intermediary thione *S*-oxides (sulfines) were not detected through NMR monitoring of the reaction of **5a** and *m*CPBA in an NMR tube at all.[9] Standing of **13a** under an aerobic condition at rt for a long time also caused gradual decomposition to afford the complex mixture containing pivalaldehyde (**3a**), *N,N*-dimethylthiourea (**1**), and a trace amount of 1,2,4-thiadiazole **14** bearing two *N,N*-dimethylamino

groups at the C-3 and C-5 positions.[10] Compound **1** was assumed to be formed from **13a** through oxidative S-O bond cleavage and the subsequent hydrolytic cleavage, and compound **14** was recognized to be an oxidative dimerization product from thiourea **1**.[2] Therefore, it is assumed that these results supported the structure of the compound to be 5*H*-1,2,4-oxathiazole ring arrangement of sulfur and oxygen atoms in the ring system of the product and the alternative pathway involving the formation of oxathiirane intermediate to form 3*H*-1,2,4-oxathiazole ring was excluded.[11]

A similar treatment of a $CHCl_3$ solution of **5a-e** with chloramine-T (1.5 mol amt.) at 0 °C to rt for 24-48 h afforded 2,3-dihydro-1,2,4-thiadiazoles **15a-e** in moderate to high yields as sole products, and in these cases any other byproducts assignable to thione *S*-imides were not found at all in the crude mixture.[12] All physical and spectral data of **15a-e** involving MS, IR, ^{1}H NMR, and ^{13}C NMR spectra, as well as the elemental analysis data, were fully consistent with the desired 2,3-dihydro-1,2,4-thiadiazole derivatives. On the other hand, **5f** was unreactive to chloramine-T, and a similar treatment of isomeric heterodiene **6** ($R^1 = C_6H_5$, $R^2 = NMe_2$) with chloramine-T just afforded 1,3-diazadiene **16** in 46% yield along with the formation of elemental sulfur. All the results of the reactions of 1,3-thiaza-1,3-butadienes **5** and **6** with chloramine-T are summarized in Table 2. Especially, standing of **13a** and **15e** under an aerobic exposure at rt for a long time caused gradual decomposition to afford the complex mixture containing aldehyde **3a** or **3e**, *N,N*-dimethylthiourea (**1**), and a trace amount of 1,2,4-thiadiazole **14** as shown in Scheme 3. It is assumed that these products were also formed through hydrolytic cleavage of **15**, and, therefore, the isomeric structure of these compounds, as 4,5-dihydro-1,2,4-thiadiazole ring system, was excluded through these results.

Table 2. Reaction of 1,3-Thiaza-1,3-butadienes **5**, **6** with *m*CPBA or Chloramine-T



5 ($R^1 = NMe_2$)
6 ($R^1 = C_6H_5$)

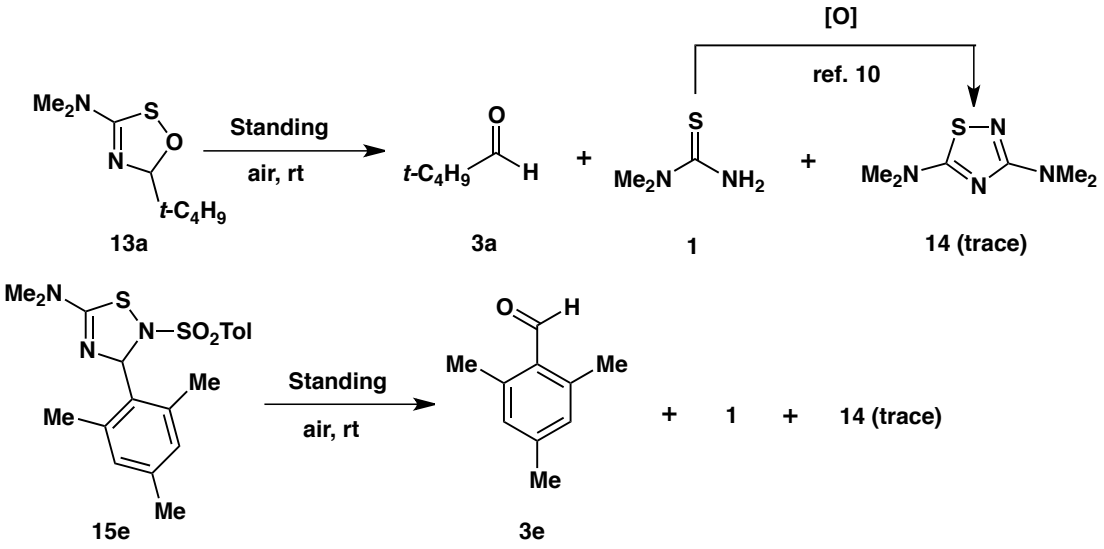
13 (X = O)
15 (X = NTs)

16

Substrate	Oxidizing Agent	Solvent	Temp	Time	Yield / %[a]		
5	(mol amt.)		/ °C	/ h	**13**, **15**	**16**	Recovery
5a	*m*CPBA (1.5)[b]	$CHCl_3$	rt	48	56 (**13a**)	0	0
5b	*m*CPBA (1.5)[b]	$CHCl_3$	0	5	complex mixture		
5c	*m*CPBA (1.5)[b]	$CHCl_3$	0	5	complex mixture		
5a	Chloramine-T (1.5)	$CHCl_3$	0	48	47 (**15a**)	0	0
5a	Chloramine-T (1.5)	$CHCl_3$	rt	48	56 (**15a**)	0	0
5b	Chloramine-T (1.5)	$CHCl_3$	rt	24	63 (**15b**)	0	0
5c	Chloramine-T (1.5)	$CHCl_3$	rt	24	52 (**15c**)	0	0
5d	Chloramine-T (1.5)	$CHCl_3$	rt	48	72 (**15d**)	0	0

5e	Chloramine-T (1.5)	$CHCl_3$	rt	24	53 (**15e**)	0	0
5f	Chloramine-T (1.5)	$CHCl_3$	rt	24	0	0	quant.
6	Chloramine-T (1.5)	$CHCl_3$	rt	48	0	46	0

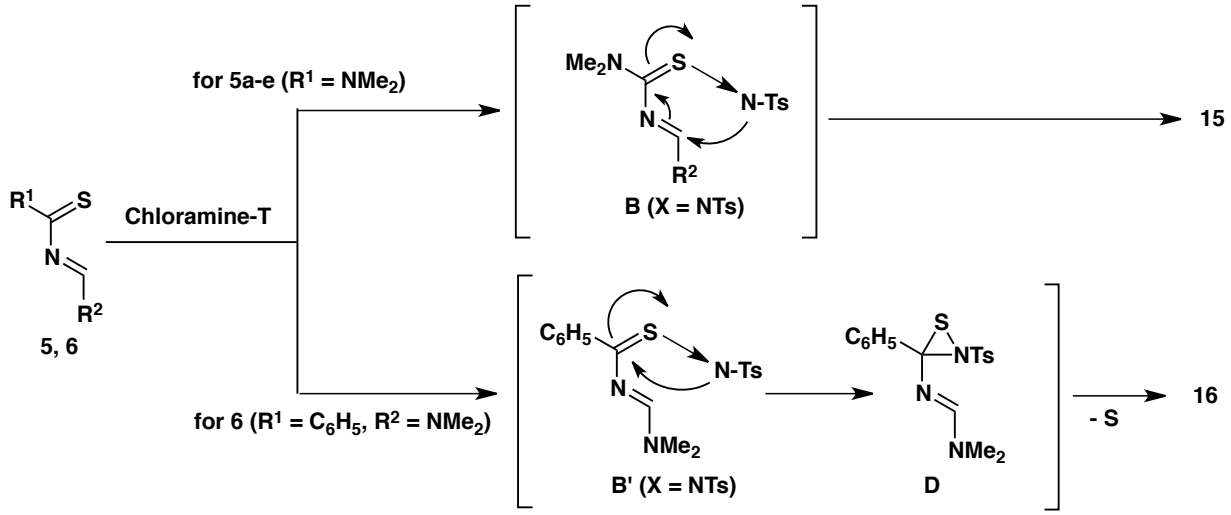
[a]Isolated yields. [b]Commercially available *m*CPBA containing 30% water was used.



Scheme 3. Standing of **13a** and **15e** under an Aerobic Condition

Subsequently, direct observation of reactive intermediates of the reaction of the heterodienes with chloramine-T was attempted. When a $CDCl_3$ solution of heterodiene **5a** (R^1 = NMe_2, R^2 = *t*-C_4H_9) was treated with chloramine-T (1.5 mol amt.) in an NMR tube and the reaction was monitored by measuring ^{1}H NMR spectra of the reaction mixture at room temperature, only the ^{1}H NMR signals of substrate **5a**, chloramine-T, and the product **15a** revealed as soon as adding chloramine-T to the solution, and no signals assignable to 1,3-thiaza-1,3-butadiene *S*-imide **B** (X = NTs) were observed in the ^{1}H NMR spectra at all both in the case of a short reaction time and the case of a prolonged reaction time. These results suggested that intermediary 1,3-thiaza-1,3-butadiene *S*-imides **B** (X = NTs) underwent facile ring closure to form **15** through the nucleophilic attack of the nitrogen atom of the intermediates onto the C-4 position of the heterodienes as shown in Scheme 4.[13] In contrast, a similar treatment of isomeric heterodiene **6** (R^1 = C_6H_5, R^2 = NMe_2) with chloramine-T just afforded 1,3-diazadiene **16** in 46% yield along with the formation of elemental sulfur, and ring closure product **15** was not found at all in the crude products. This result indicated that compound **16** was formed through sulfonylimidation of 1,3-thiaza-1,3-butadienes primarily at the sulfur atom of heterodiene **6** forming 1,3-thiaza-1,3-butadiene *S*-imide **B** (X = NTs) and the subsequent ring closure of **B** and the final extrusion of elemental sulfur from the thiaziridine intermediate **D**[14] as shown in Scheme 4. The lack of ring closure products in this case was explained by the low feasibility of the C-4 position of the heterodienes bearing an *N,N*-dimethylamino group at the C-4 position of **6** toward the intramolecular nucleophilic attack of the nitrogen atom due to the

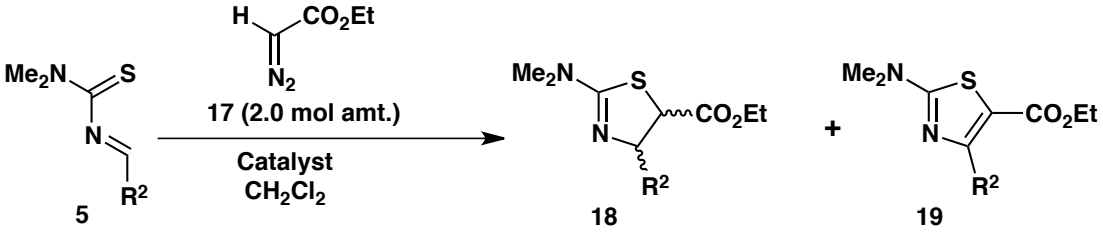
electron-donating character of the *N,N*-dimethylamino group bound directly onto the azomethine carbon of the heterodienes.



Scheme 4. Plausible Pathways for the Formation of Compounds **15** and **16** through the Reaction of Heterodienes **5** or **6** with Chloramine-T

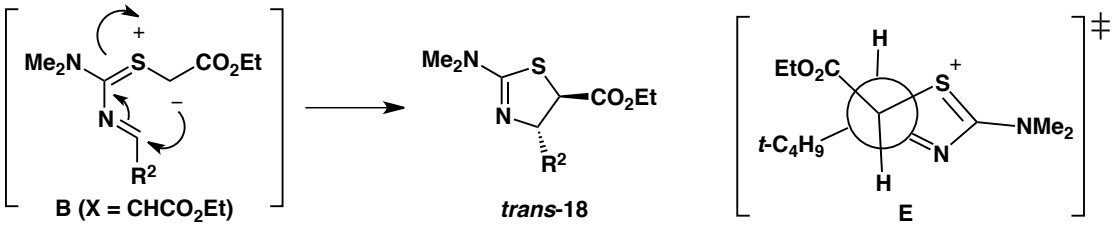
A similar treatment of a CH_2Cl_2 solution of heterodienes **5a** or **5e** with ethyl diazoacetate (**17**, 1.5 mol amt.) in the presence of Cu_2Cl_2 (1.5 mol amt.) or $Rh_2(OAc)_4$ (0.01 mol amt.) at rt afforded *cis*/*trans* mixtures of 4,5-dihydro-1,3-thiazoles **18** bearing an ester moiety at the C-5 position and 1,3-thiazoles **19a** or **19e**, respectively, in moderate yields. The *trans* stereochemistry of **18a** and **18e** between the *t*-butyl or mesityl goup on the C-4 and the ester moiety at the C-5 position was confirmed by using an NOE experiment of the compounds, and, for instance, the 7% NOE was observed between the *t*-butyl group at the C-4 position and the methane proton at the C-5 position in the case of *trans*-**18a**. It is assumed that the predominant formation of *trans*-**18** would be rationalized by the plausible pathway involving more favorable transition state **E** with a less steric repulsion of the substituents in the stage of ring closure of intermediary thiocarbonyl ylide **B** formed through the reaction of **5** with ethyl diazoacetate (**17**) and $Rh_2(OAc)_4$ as shown in Scheme 5. In addition, it is worth noting that neither isomeric heterocyclic compounds nor acyclic isomeric products or desulfurized olefinic products were found at all in the crude products.[15] All the results of the synthesis of 4,5-dihydro-1,3-thiazoles **18** and 1,3-thiazoles **19** are shown in Table 3. Dehydrogenation of a *cis*/*trans* mixture of **18e** was also achieved efficiently by treating with DDQ (2.0 mol amt.) to give thiazole **19e** in 65% yield as a sole product as shown in Scheme 6. Furthermore, ethyl ester **19b** ($R^2 = C_6H_5$, $R^3 = CO_2Et$) was hydrolyzed through a usual manner to give the corresponding free carboxylic acid.[16] In contrast, a similar treatment of heterodiene **6** ($R^1 = C_6H_5$, $R^2 = NMe_2$) with ethyl diazoacetate and Cu_2Cl_2 just resulted in the formation of a complex mixture.

Table 3. Synthesis of 4,5-Dihydro-1,3-thiazoles **18** and 1,3-Thiazoles **19** through the Reaction of 1,3-Thiaza-1,3-butadienes **5** with Metal Carbenoids

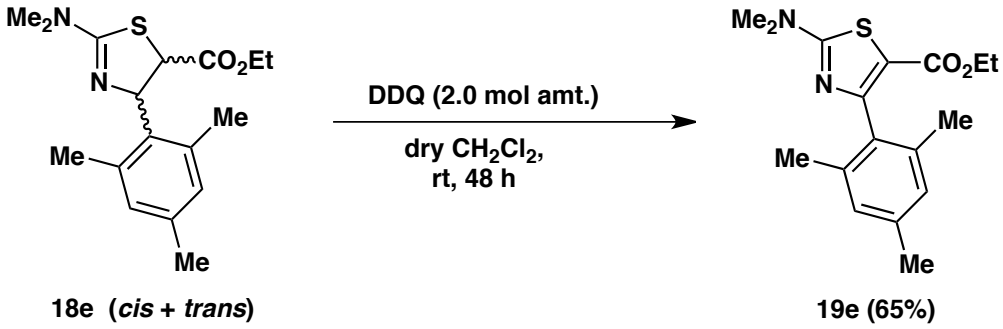


Substrate		Catalyst	Temp	Time	Yield / % [a]			
R^2	**5**	(mol amt.)	/ °C	/ h	*trans*-**18**[b]	*cis*-**18**[b]	**19**	Recovery
t-C_4H_9	**5a**	Cu_2Cl_2 (1.5)	rt	48	45 (**18a**)	0	0	trace[c]
t-C_4H_9	**5a**	$Rh_2(OAc)_4$ (0.01)	rt	120	63 (**18a**)	0	0	30
C_6H_5	**5b**	Cu_2Cl_2 (1.5)	rt	1	0	0	20 (**19b**)	trace[c]
C_6H_5	**5b**	$Rh_2(OAc)_4$ (0.01)	rt	72	0	0	0	quant.
Mes	**5e**	Cu_2Cl_2 (2.0)	rt	36	27 (**18e**)	6 (**18e**)	5	trace[c]
NMe_2	**5f**	Cu_2Cl_2 (2.0)	reflux	48	0	0	30 (**19f**)[d]	trace[c]

[a]Isolated yields. [b]The relative stereochemistry of *trans*-**18** and *cis*-**18** concerning the substituents of the C-4 and C-5 positions was confirmed through the NOE experiments. [c]A complex mixture was obtained. [e d]Compound **19f** (R^2 = H)[17] was obtained.



Scheme 5. Plausible Pathway for the Ring Closure of Thiocarbonyl Ylides **B** (X = $CHCO_2Et$)

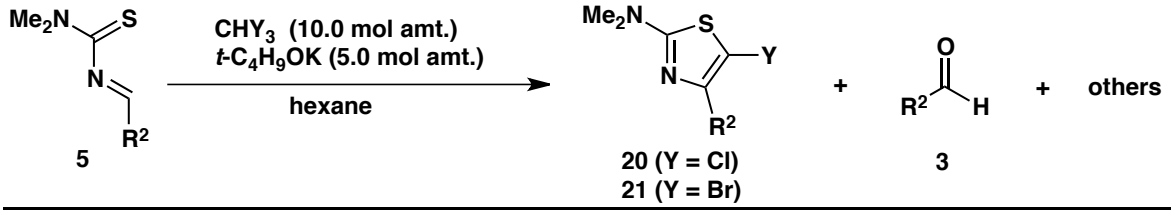


Scheme 6. Dehydrogenation of **18e** to form 1,3-Thiazole **19e**

When a hexane solution of **5a** or **5e** was treated with $CHCl_3$ (10.0 mol amt.) and then with potassium *t*-butoxide (5.0 mol amt.) at 0 °C for several hours, the corresponding 1,3-thiazoles **20a** (Y = Cl) and **20e** (Y = Cl) were afforded beside aldehydes **3a** and **3e**, respectively, among several uncharacterized byproducts. However, in spite of the efforts of optimization of the experimental procedures and reaction conditions, the yields of compounds **20** remained in a moderate level, and neither the recovered substrates **5** nor the precursory 5,5-dichloro-4,5-dihydro-1,3-thiazole (**F**) was not found in the crude mixture in all

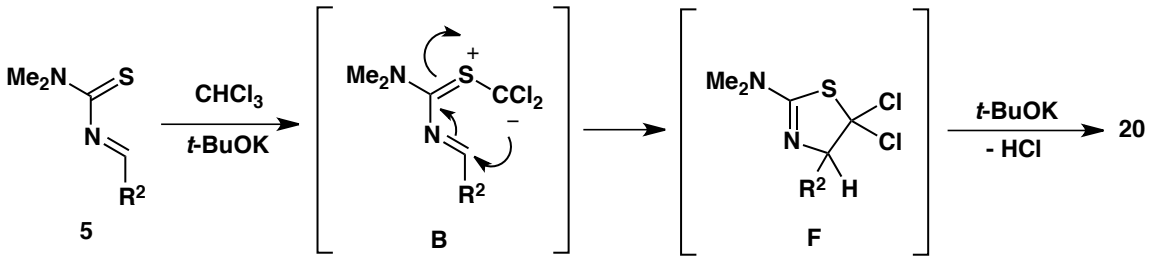
cases. 5-Chloro-1,3-thiazoles **20** were assumed to form through a plausible pathway involving the ring closure of *in situ* generation of thiocarbonyl ylides **B**[15f,18] and the subsequent dehydrochlorination of ring closure product **F** under a basic condition as shown in Scheme 7. In contrast, a similar treatment of **5e** with $CHBr_3$ in place of $CHCl_3$ at 0 °C or -78 °C only afforded aldehyde **3e** or a complex mixture, and 5-bromo-1,3-thiazole **21e** (Y = Br) was not found at all in the crude reaction mixture. All the results of the reaction of 1,3-thiaza-1,3-butadienes **5** with *in situ* generated dichlorocarbene forming 5-chloro-1,3-thiazoles **20** are shown in Table 4. Alternative attempts for the conversion of **5e** into 5-phenyl-1,3-thiazoles by treating with benzal chloride ($C_6H_5CHCl_2$) and potassium *t*-butoxide in a similar manner just resulted in the formation of aldehyde **3e** in all cases.

Table 4. Reaction of 1,3-Thiaza-1,3-butadienes **5** with *in situ* Generated Dihalocarbenes



Substrate		Haloform	Temp	Time	Yield / %[a]		
R^2	**5**	Y	/ °C	/ h	**20**	**21**	**3**
t-C_4H_9	**5a**	Cl	0	3	16 (**20a**)	-	10 (**3a**)
Mes	**5e**	Cl	0	5	25 (**20e**)	-	15 (**3e**)
Mes	**5e**	Br	0	3	-	complex mixture	
Mes	**5e**	Br	-78	3	-	0	87 (**3e**)

[a]Isolated yields.



Scheme 7. Plausible Pathway for the Formation of 5-Chloro-1,3-thiazoles **20**

CONCLUSION

In conclusion, we found a generation and the subsequent facile ring closure of novel heterocumulene-type oxidized variants of 1,3-thiaza-1,3-butadienes **5** to afford 5*H*-1,2,4-oxathiazoles, 2,3-dihydro-1,2,4-thiadiazoles, 4,5-dihydro-1,3-thiazoles, and 1,3-thiazoles. It is recognized that these methodology afford a new and convenient synthetic protocol for the short step synthesis of naturally occurring and biologically active 1,3-thiazole derivatives. Further attempts for the conversion of the products of oxidative ring closure of 1,3-thiaza-1,3-butadienes **5** into various pharmaceutically active compounds are expected in our laboratory.

EXPERIMENTAL SECTION

Instruments:

The melting points were determined with a Barnstead International MEL-TEMP, and were uncorrected. ^{1}H NMR spectra were recorded on a Bruker DRX 400-P spectrometer (400 MHz), and the chemical shifts of the ^{1}H NMR spectra are given in δ relative to internal tetramethylsilane (TMS). ^{13}C NMR spectra were recorded using a Bruker DRX-400P (101 MHz). Mass spectra were recorded on a JEOL JMS-700T mass spectrometer with electron-impact ionization or electrospray ionization. High resolution mass spectra (HRMS) were also recorded on a JEOL JMS-700T spectrometer. IR spectra were measured as thin-film (neat) or KBr disks on a JASCO FT/IR-7300 spectrometer. Elemental analyses were performed using a Yanagimoto CHN corder MT-5.

Starting Materials. Column chromatography was performed using silica gel (Merck, Cat. No. 7734 or 9385) without pretreatment. Dichloromethane (CH_2Cl_2) and chloroform ($CHCl_3$) were dried over P_4O_{10} and were freshly distilled before use. Hexane, benzene, toluene, and EtOAc were dried over CaH_2 and were freshly distilled before use. Ethanol was dried over MgO and was freshly distilled before use. All substrates and reagents including pivalaldehyde, benzaldehyde, *p*-chlorobenzaldehyde, 2,4,6-trimethylbenzaldehyde, cinnamaldehyde, thiobenzamide, triethylamine, boron trifluoride diethyl ether complex (BF_3•OEt_2), iron sulfide (Fe(II)S), hydrochloric acid, *N,N*-dimethylcyanamide, *N,N*-dimethylformamide dimethyl acetal, *m*-chloroperbenzoic acid (*m*CPBA, 70%), chloramine-T, elemental sulfur, ethyl diazoacetate (15% toluene solution), methyl propiolate, dimethyl acetylenedicarboxylate (DMAD), copper(I) chloride (Cu_2Cl_2), rhodium acetate ($Rh_2(OAc)_4$), 2,3-dichloro-2,3-dicyano-1,4-benzoquinone (DDQ), benzal chloride, potassium *t*-butoxide (*t*-C_4H_9OK), and anhydrous sodium sulfate powder (Na_2SO_4) were commercially available reagent grade and were used without any pretreatment.

A Typical Procedure for the Preparation of 1,3-Thiaza-1,3-butadienes 5. A dry $CHCl_3$ solution of *N,N*-dimethylthiourea **1** (80 mg, 0.77 mmol) was treated with pivalaldehyde (**3a**, 190 mg, 4.0 mol amt.) and boron trifluoride diethyl ether complex (BF_3•OEt_2) (350 mg, 3.2 mol amt.) at rt for 12 h. The reaction was quenched by addition of an aqueous $NaHCO_3$ solution, and the reaction mixture was extracted with $CHCl_3$. The organic layer was dried over anhydrous Na_2SO_4 powder, and then the organic solvent was evaporated *in vacuo* to obtain 1,3-thiaza-1,3-butadiene **5a** (R^1 = NMe_2, R^2 = *t*-C_4H_9, 276 mg, 93% yield) as yellow oil.

5a (R^1 = NMe_2, R^2 = *t*-C_4H_9): Yellow oil, MS (*m/z*) 172 (M^+; 45%), 140 (M^+-S; 5%), 115 (M^+-*t*-C_4H_9; 13%), 89 (Me_2NCS+1; bp), 44 (NMe_2; 95%); IR (neat) 2961, 2934, 2868, 1658, 1526, 1125 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.15 (9H, s), 3.25 (3H, s), 3.47 (3H, s), 8.19 (1H, s); ^{13}C NMR ($CDCl_3$) δ 26.2 (q), 37.1

(s), 40.0 (q), 43.5 (q), 177.3 (d), 194.2 (s). Anal. Calcd for $C_8H_{16}N_2S$: C, 54.30; H, 9.85, N, 12.76%. Found: C, 54.18; H, 9.75; N, 12.83%.

5b (R^1 = NMe_2, R^2 = C_6H_5): Orange oil; MS (*m/z*) 192 (M^+; bp), 148 (M^+-NMe_2; 28%), 89 (Me_2NCS+1; 47%); IR (neat) 2931, 1630, 1522, 1122, 759, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.38 (3H, s), 3.55 (3H, s), 7.48 (2H, br. t, *J* = 7.4 Hz), 7.55 (1H, br. t, *J* = 7.4 Hz), 7.90 (2H, br. t, *J* = 7.4 Hz), 8.99 (1H, s); ^{13}C NMR ($CDCl_3$) δ 40.3 (q), 43.7 (q), 128.9 (d), 130.2 (d), 133.1 (d), 134.6 (s), 165.6 (d), 193.6 (s). HRMS Calcd for $C_{10}H_{12}N_2S$: *m/z* 192.0721. Found: *m/z* 192.0715.

5c (R^1 = NMe_2, R^2 = *p*-ClC_6H_4): Orange oil; MS (*m/z*) 226 (M^+; bp), 89 (Me_2NCS+1; 68%); IR (neat) 3164, 2924, 1623, 1527, 1398, 1269, 1087, 864, 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.38 (3H, s), 3.55 (3H, s), 7.55 (2H, d, *J* = 8.4 Hz), 7.85 (2H, d, *J* = 8.4 Hz), 8.96 (1H, s); ^{13}C NMR ($CDCl_3$) δ 40.3 (q), 43.7 (q), 129.3 (d), 131.3 (d), 133.1 (s), 139.3 (s), 164.4 (d), 193.2 (s). HRMS Calcd for $C_{10}H_{11}N_2SCl$: *m/z* 226.0331. Found: *m/z* 226.0329.

5d (R^1 = NMe_2, R^2 = C_6H_5CH=CH): Orange oil; MS (*m/z*) 218 (M^+; bp), 115 (M^+-C_6H_5CH=CH; 28%), 89 (Me_2NCS+1; 81%); IR (neat) 2927, 1674, 1615, 1525, 1274, 1122, 759, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.34 (3H, s), 3.52 (3H, s), 7.01 (1H, dd, *J* = 16.0, 9.6 Hz), 7.36 (1H, d, *J* = 16.0 Hz), 7.38-7.45 (3H, m), 7.54-7.58 (2H, m), 8.78 (1H, br. d, *J* = 9.6 Hz); ^{13}C NMR ($CDCl_3$) δ 39.1 (q), 42.6 (q), 127.0 (d), 128.0 (d), 129.4 (d), 134.0 (s), 148.0 (d), 151.8 (d), 166.4 (d), 192.5 (s). HRMS Calcd for $C_{12}H_{14}N_2S$: *m/z* 218.0878. Found: *m/z* 218.0877.

5e (R^1 = NMe_2, R^2 = Mes): Yellow oil; MS (*m/z*) 234 (M^+; bp), 146 (MesCNH; 57%), 89 (Me_2NCS+1; 68%); IR (neat) 2923, 1606, 1518, 1454, 1387, 1274, 1115 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.24 (3H, s), 2.51 (6H, s), 3.30 (3H, s), 3.48 (3H, s), 6.84 (2H, s), 9.45 (1H, s); ^{13}C NMR ($CDCl_3$) δ 20.4 (q), 20.9 (q), 39.5 (q), 42.8 (q), 45.8 (q), 130.3 (d), 140.3 (s), 165.3 (d), 193.4 (s). HRMS Calcd for $C_{13}H_{18}N_2S$: *m/z* 234.1191. Found: *m/z* 234.1183.

A Typical Procedure for the Reaction of 1,3-Thiaza-1,3-butadienes 5 with Ethanol. An ethanolic solution of 1,3-thiaza-1,3-butadiene **5a** (R^1 = NMe_2, R^2 = *t*-C_4H_9, 86 mg, 0.50 mmol) was heated under refluxing temperature for 5 h. The reaction mixture was cooled and the solvent was evaporated *in vacuo*. The crude mixture was separated by using chromatography on silica gel to obtain compound **7a** (21 mg, 24% yield) as yellow oil.

7a (R^1 = NMe_2, R^2 = *t*-C_4H_9): Yellow oil; MS (*m/z*) 218 (M^+; 56%), 172 (M^+-EtOH; 11%), 88 (Me_2NCS; 43%); IR (neat) 2960, 1526, 1344, 1069 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (9H, s), 1.17 (3H, t, *J* = 7.0 Hz), 3.31 (6H, s), 3.60 (1H, dq, *J* = 10.0, 7.0 Hz), 3.70 (1H, dq, *J* = 10.0, 7.0 Hz), 5.53 (1H, br. d, *J* = 8.5 Hz), 5.66 (1H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 15.2 (q), 25.3 (q), 36.2 (q), 40.5 (q), 64.1 (t), 91.3 (d),

182.4 (s). Anal. Calcd for $C_{10}H_{22}N_2OS$: C, 55.00; H, 10.16; N, 12.83%. Found: C, 54.56; H, 10.33; N, 12.60%.

7b (R^1 = NMe_2, R^2 = C_6H_5): Yellow oil; IR (neat) 2960, 1526, 1370, 1116, 1069 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (3H, t, *J* = 7.0 Hz), 3.29 (6H, s), 3.72 (1H, dq, *J* = 10.0, 7.0 Hz), 3.86 (1H, dq, *J* = 10.0, 7.0 Hz), 5.80 (1H, d, *J* = 8.5 Hz), 6.94 (1H, d, *J* = 8.5 Hz), 7.30-7.40 (2H, m), 7.40-7.60 (3H, m); ^{13}C NMR ($CDCl_3$) δ 15.2 (q), 40.3 (q), 43.7 (q), 64.1 (t), 85.8 (d), 126.0 (d), 128.3 (d), 130.2 (d), 140.1 (s), 181.7 (s). Anal. Calcd for $C_{12}H_{18}N_2OS$: C, 60.47; H, 7.61; N, 11.75%. Found: C, 60.01; H, 7.46; N, 11.64%.

A Typical Procedure for the Reaction of 1,3-Thiaza-1,3-butadienes 3 with an Acetylenic Dienophile. A toluene solution of 1,3-thiaza-1,3-butadiene **3a** (R^1 = NMe_2, R^2 = *t*-C_4H_9, 90 mg, 0.52 mmol) was treated with methyl propiolate (**8a**, R^3 = H, 132 mg, 1.57 mmol, 3.0 mol amt.) under refluxing temperature for 1 h. The reaction mixture was cooled and the solvent was evaporated *in vacuo*. The crude mixture was separated by using chromatography on silica gel to obtain [4+2] cycloadduct **9a** (93 mg, 71% yield) as yellow oil.

9a (R^1 = NMe_2, R^2 = *t*-C_4H_9, R^3 = H, R^4 = CO_2Me): Yellow oil; MS (*m/z*) 257 (M^++1; bp), 199 (M^+-*t*-C_4H_9; 1%); IR (neat) 2951, 2374, 1702, 1632, 1593, 1327, 1195 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (9H, s), 3.01 (6H, s), 3.74 (3H, s), 4.66 (1H, s), 5.97 (1H, s); ^{13}C NMR ($CDCl_3$) δ 26.4 (q), 36.3 (q), 39.5 (q), 51.6 (q), 87.9 (d), 108.9 (d), 159.4 (s), 165.8 (s), 166.0 (s). Anal. Calcd for $C_{12}H_{20}N_2O_2S$: C, 56.22; H, 7.86; N, 10.93%. Found: C, 55.91; H, 7.65; N, 10.81%.

10a (R^1 = NMe_2, R^2 = *t*-C_4H_9, R^3 = R^4 = CO_2Me): Yellow oil; MS (*m/z*) 315 (M^++1; bp), 257 (M^+-*t*-C_4H_9; 21%); IR (neat) 2952, 1726, 1635, 1434, 1363, 1134, 1257, 1039, 734 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (9H, s), 3.01 (6H, s), 3.76 (3H, s), 3.82 (3H, s), 4.78 (1H, s); ^{13}C NMR ($CDCl_3$) δ 26.6 (q), 38.8 (q), 41.5 (s), 52.4 (q), 53.1 (q), 69.2 (d), 130.0 (s), 131.6 (s), 148.6 (s), 164.8 (s), 167.9 (s). HRMS (CI) Calcd for $C_{12}H_{14}N_2O_4S$: *m/z* 314.1300. Found: *m/z* 315.1381 (M^++1). Anal. Calcd for $C_{14}H_{22}N_2O_4S$: C, 53.48; H, 7.05; N, 8.91%. Found: C, 53.02; H, 6.88; N, 8.78%.

11a (R^1 = NMe_2, R^2 = R^3 = *t*-C_4H_9, R^4 = $COCO_2Et$): Yellow oil; MS (*m/z*) 355 (M^+; bp), 297 (M^+-C_4H_{10}; 21%); IR (neat) 2957, 1727, 1600, 1457, 1365, 1134, 719 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11 (9H, s), 1.30 (3H, t, *J* = 7.2 Hz), 1.41 (9H, s), 2.68 (6H, s), 3.95 (1H, s), 4.21 (2H, q, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 27.0 (q), 28.4 (q), 34.9 (q), 40.7 (q), 40.9 (s), 61.6 (t), 77.2 (d), 121.0 (s), 164.6 (s), 165.4 (s), 180.7 (s), 189.1 (s). HRMS Calcd for $C_{18}H_{31}N_2O_3S$: *m/z* 355.2055. Found: *m/z* 355.2067.

Preparation of Thiobenzamide 12 from Heterodiene 5f and Methyl Propiolate (8a). A $CHCl_3$ solution of 1,3-thiaza-1,3-butadiene **5f** (R^1 = NMe_2, R^2 = NMe_2, 100 mg, 0.63 mmol) was treated with methyl propiolate (**8a**, R^3 = H, 79 mg, 0.94 mmol, 1.5 mol amt.) at rt for 5 days. The reaction mixture was

cooled and the solvent was evaporated *in vacuo*. The crude mixture was separated by using chromatography on silica gel to obtain thioenamide **12** (37 mg, 27% yield) as yellow oil besides the recovery of **3a** (47 mg, 48% yield).

12: Yellow oil; MS (*m/z*) 216 (M^+: 4%), 187(M^+-CHO; bp), 89 (Me_2NCS+1; 20%); IR (neat) 3486, 2949, 2377, 1716, 1532, 1241, 779 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.42 (3H, s), 3.58 (3H, s), 3.85 (3H, s), 9.13-9.22 (1H, m), 10.0 (1H, d, *J* = 4.0 Hz), 13.1 (1H, br. s); ^{13}C NMR ($CDCl_3$) δ 39.6 (q), 44.3 (q), 51.8 (s), 106.4 (s), 152.9 (d), 166.3 (s), 179.2 (s), 193.5 (d). HRMS Calcd for $C_8H_{12}N_2OS$: *m/z* 216.0569. Found: *m/z* 216.0571 (M^++1).

A Typical Procedure for the Reaction of 1,3-Thiaza-1,3-butadienes 5 with *m*CPBA. A $CHCl_3$ solution of 1,3-thiaza-1,3-butadiene **5a** (R^1 = NMe_2, R^2 = *t*-C_4H_9, 122 mg, 0.71 mmol) was treated with *m*CPBA (70%, 260 mg, 1.5 mol amt.) and $NaHCO_3$ powder (100 mg, 2.0 mol amt.) at rt for 48 h. The reaction was quenched by addition of an excess amount of saturated Na_2SO_3 solution, and the reaction mixture was extracted with $CHCl_3$. The organic layer was dried over anhydrous Na_2SO_4 powder, and then the organic solvent was evaporated *in vacuo*. The crude products were separated by using chromatography on silica gel to obtain 5*H*-1,2,4-oxathiazole **13a** (76 mg, yield 56%) as colorless oil.

13a (R^1 = NMe_2, R^2 = *t*-C_4H_9): Colorless oil; MS (*m/z*) 156 (M^+-S; 53%), 139 (M^+-SOH; bp), 57 (*t*-C_4H_9; 68%); IR (neat) 2960, 2935, 2876, 1668, 1126 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97 (9H, s), 3.16 (6H, s), 6.20 (1H, s); ^{13}C NMR ($CDCl_3$) δ 25.1 (q), 35.6 (s), 39.3 (q), 123.3 (d), 165.0 (s). Anal. Calcd for $C_8H_{16}N_2OS$: C, 51.03; H, 8.56; N, 14.88%. Found: C, 50.54; H, 8.21; N, 14.67%.

A Typical Procedure for the Reaction of 1,3-Thiaza-1,3-butadienes 5 with Chloramine-T. A $CHCl_3$ solution of 1,3-thiaza-1,3-butadiene **5a** (R^1 = NMe_2, R^2 = *t*-C_4H_9, 76 mg, 0.44 mmol) was treated with chloramine-T (0.189 g, 1.5 mol amt.) at rt for 48 h. The reaction was quenched by addition of an excess amount of water, and the reaction mixture was extracted with $CHCl_3$. The organic layer was dried over anhydrous Na_2SO_4 powder, and then the organic solvent was evaporated *in vacuo*. The crude crystalline solids were purified by using chromatography on silica gel and the subsequent recrystallization from $CHCl_3$-EtOAc to obtain 2,3-dihydro-1,2,4-thiadiazole **15a** (20 mg, yield 56%) as colorless prisms.

15a (R^1 = NMe_2, R^2 = *t*-C_4H_9): Colorless prisms, mp 185.1-188.2 °C; MS (*m/z*) 284 (M^+-*t*-C_4H_9; bp), 155 (M^+-*p*-$TolSO_2$; 85%), 91 (Tol; 90%); IR (KBr) 2964, 2929, 2869, 1644, 1344, 1165, 809 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (9H, s), 2.41 (3H, s), 2.70 (6H, s), 5.58 (1H, s), 7.27 (2H, br. d, *J* = 8.0 Hz), 7.78 (2H, br. d, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 21.5 (q), 26.3 (q), 39.8 (q), 39.9 (s), 101.7 (d), 129.0 (d), 129.3 (d), 130.9 (s), 144.2 (s), 160.4 (s). Anal. Calcd for $C_{15}H_{23}N_3O_2S_2$: C, 52.50; H, 6.72; N, 11.83%. Found: C, 52.76; H, 6.79; N, 12.30%.

15b (R^1 = NMe_2, R^2 = C_6H_5): Colorless prisms, mp 122.3-124.8 °C; MS (*m/z*) 361 (M^+; 10%), 291 (M^+-Me_2NCN; 5%), 227 (M^+-$Me_2NCNC_6H_5$; bp), 206 (M^+-*p*-$TolSO_2$; 27%), 91 (Tol; 59%); IR (KBr) 2959, 2927, 2900, 1641, 1345, 1167, 816, 768, 679 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.45 (3H, s), 2.75 (6H, s), 7.02 (1H, s), 7.31-7.33 (5H, m), 7.46-7.47 (2H, m), 7.86 (2H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 21.7 (q), 40.1 (q), 93.1 (d), 126.6 (d), 128.1 (d), 128.5 (d), 129.0 (d), 129.3 (d), 131.3 (s), 137.5 (s), 144.8 (s), 162.3 (s). Anal. Calcd for $C_{17}H_{19}N_3O_2S$: C, 56.48; H, 5.30; N, 11.62%. Found: C, 56.36; H, 5.19; N, 11.63%.

15c (R^1 = NMe_2, R^2 = *p*-ClC_6H_4): Colorless needles, mp 156.3-157.6 °C; IR (KBr) 2918, 2326, 1627, 1345, 1160, 1052, 558 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.46 (3H, s), 2.78 (3H, s), 6.97 (1H, s), 7.30 (2H, d, *J* = 8.4 Hz), 7.34 (2H, d, *J* = 8.4 Hz), 7.41 (2H, d, *J* = 8.4 Hz), 7.86 (2H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 21.7 (q), 40.4 (q), 91.7 (d), 126.5 (d), 128.2 (d), 128.3 (d), 129.1 (d), 129.4 (d), 129.7 (d), 131.1 (s), 134.4 (s), 135.8 (s), 145.0 (s), 161.2 (s). Anal. Calcd for $C_{17}H_{18}ClN_3O_2S_2$: C, 51.57; H, 4.58; N, 10.61%. Found: C, 51.94; H, 4.41; N, 10.18%.

15d (R^1 = NMe_2, R^2 = C_6H_5CH=CH): Yellow oil; MS (*m/z*) 388 (M^++1; bp), 317 (M^+-Me_2NCN; 33%), 232 (M^+-*p*-$TolSO_2$; 48%), 162 (M^+-*p*-$TolSO_2$-Me_2NCN; 37%); IR (neat) 2984, 1694, 1630, 1522, 1261, 1081, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.43 (3H, s), 2.71 (6H, s), 6.11 (1H, d, *J* = 16.0 Hz), 6.56 (1H, dd, *J* = 4.8, 1.2 Hz), 6.64 (1H, d, *J* = 0.8 Hz), 7.22-7.25 (1H, m), 7.29-7.31 (4H, m), 7.37 (2H, d, *J* = 7.2 Hz), 7.83 (2H, d, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 21.6 (q), 40.1 (q), 92.5 (d), 124.3 (d), 126.9 (d), 128.0 (d), 128.5 (d), 128.9 (d), 129.4 (d), 131.3 (s), 132.1 (d), 136.0 (s), 144.7 (s), 161.9 (s). HRMS Calcd for $C_{19}H_{21}N_3O_2S_2$: *m/z* 387.1075. Found: *m/z* 388.1160 (M^++1).

15e (R^1 = NMe_2, R^2 = Mes): Yellow prisms, mp 164.2-166.5 °C; IR (KBr) 2921, 2379, 1937, 1384, 1350, 1160, 666 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.16 (3H, s), 2.38 (3H, s), 2.42 (6H, s), 2.69 (6H, s), 6.75 (2H, s), 7.06 (1H, s), 7.22 (2H, d, *J* = 8.0 Hz), 7.79 (2H, d, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 20.8 (q), 21.2 (q), 21.7 (q), 39.7 (q), 93.4 (d), 129.4 (d), 129.7 (d), 130.6 (d), 131.5 (s), 132.3 (s), 137.2 (s), 137.8 (s), 144.6 (s), 158.8 (s). Anal. Calcd for $C_{20}H_{25}N_3O_2S_2$: C, 59.52; H, 6.24; N, 10.41%. Found: C, 59.10; H, 6.21; N, 10.23%.

Procedure for the Reaction of 1,3-Thiaza-1,3-butadiene 6 with Chloramine-T. A $CHCl_3$ solution of 1,3-thiaza-1,3-butadiene **6** (R^1 = C_6H_5, R^2 = NMe_2, 100 mg, 0.52 mmol) was treated with chloramine-T (210 mg, 1.5 mol amt.) at rt for 48 h. The reaction was quenched by addition of an excess amount of water, and the reaction mixture was extracted with $CHCl_3$. The organic layer was dried over anhydrous Na_2SO_4 powder, and then the organic solvent was evaporated *in vacuo*. The crude crystalline solids were purified by using chromatography on silica gel and the subsequent recrystallization from $CHCl_3$-EtOAc to obtain product **16** (79 mg, yield 46%) as pale yellow needles.

16: Pale yellow needles, mp 124.3-124.8 °C; MS (*m/z*) 329 (M^+; 30%), 328 (M^+-1; 40%), 162 (M^+-NSO_2Tol; bp), 91 (M^+-$C_{10}H_{13}N_3O_2S$; 69%); IR (KBr) 2927, 2363, 2868, 1497, 1147, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.40 (3H, s), 3.15 (3H, s), 3.20 (3H, s), 7.65 (2H, t, *J* = 4 Hz), 7.36 (2H, t, *J* = 8.5 Hz), 7.46 (1H, t, *J* = 7.0 Hz), 7.88 (2H, d, *J* = 7.0 Hz), 7.93 (2H, d, *J* = 8.5 Hz), 8.04 (1H, s); ^{13}C NMR ($CDCl_3$) δ 21.5 (q), 35.2 (q), 41.2 (q), 126.7 (d), 128.1 (d), 129.0 (d), 129.6 (d), 132.0 (d), 136.6 (s), 140.4 (s), 142.1 (s), 157.7 (d), 169.9 (s). Anal. Calcd for $C_{12}H_{19}N_3O_2S$: C, 61.98; H, 5.81; N, 12.76%. Found: C, 61.77; H, 5.73; N, 12.70%.

A Typical Procedure for the Reaction of 1,3-Thiaza-1,3-butadienes 5 with Ethyl Diazoacetate in the Presence of a Catalytic Amount of $Rh_2(OAc)_4$. A CH_2Cl_2 solution of 1,3-thiaza-1,3-butadiene **5a** (R^1 = NMe_2, R^2 = *t*-C_4H_9, 93 mg, 0.54 mmol) was treated with a toluene solution of ethyl diazoacetate (0.8 mL, 1.08 mmol, 2.0 mol amt.) and a toluene solution of $Rh_2(OAc)_4$ (0.44 mg, 1.0 μmol, 0.01 mol amt.) at rt for 120 h. The solvent was removed by evaporation from the reaction mixture, and the crude mixture was separated by using chromatography on silica gel to obtain *trans*-**18a** (88 mg, 63% yield) as yellow oil.

A Typical Procedure for the Reaction of 1,3-Thiaza-1,3-butadienes 5 with Ethyl Diazoacetate in the Presence of Cu_2Cl_2. A CH_2Cl_2 solution of 1,3-thiaza-1,3-butadiene **5e** (R^1 = NMe_2, R^2 = Mes, 100 mg, 0.43 mmol) was treated with a toluene solution of ethyl diazoacetate (0.86 mmol, 2.0 mol amt.) and Cu_2Cl_2 (84 mg, 0.86 mmol, 2.0 mol amt.) at rt for 36 h. Then, the solvent was removed by evaporation from the reaction mixture, and the crude brown solid was separated by using chromatography on silica gel to obtain *trans*-**18e** (38 mg, 27% yield, yellow oil), *cis*-**18e** (8 mg, 6% yield, yellow oil), and **19e** (7 mg, 5% yield, colorless solid) as yellow oil.

trans-**18a** (R^1 = NMe_2, R^2 = *t*-C_4H_9): Yellow oil; MS (*m/z*) 258 (M^+; 14%), 201 (M^+-*t*-C_4H_9; bp); IR (neat) 2955, 1739, 1635, 1368, 1171, 1030, 605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (9H, s), 1.27 (3H, t, *J* = 7.2 Hz), 2.97 (6H, s), 4.20 (2H, q, *J* = 7.2 Hz), 4.25 (1H, d, *J* = 4.0 Hz), 4.40 (1H, d, *J* = 4.0 Hz); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 26.2 (q), 36.2 (s), 40.1 (q), 53.3 (d), 61.1 (t), 86.3 (d), 158.9 (s), 172.6 (s). HRMS Calcd for $C_{12}H_{23}N_2O_2S$: *m/z* 259.1480. Found: *m/z* 259.1482.

19b (R^1 = NMe_2, R^2 = C_6H_5)[16]: Yellow needles, 33.1-34.0 °C; MS (*m/z*) 276 (M^+; bp), 247 (M^+-C_2H_5; 28%); IR (KBr) 2925, 1740, 1630, 1353, 1164, 1086, 682 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (3H, t, *J* = 7.2 Hz), 3.18 (6H, s), 4.19 (2H, q, *J* = 7.2 Hz), 7.38-7.39 (3H, m), 7.72-7.73 (2H, m).

trans-**18e** (R^1 = NMe_2, R^2 = Mes): Yellow oil; MS (*m/z*) 320 (M^+; 54%), 247 (M^+-CO_2Et; bp); IR (neat) 2925, 1740, 1633, 1373, 1160, 1029, 661 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.77 (3H, t, *J* = 7.0 Hz), 2.20 (3H, s), 2.35 (6H, s), 3.06 (6H, s), 3.50 (1H, dq, *J* = 11.0, 7.0 Hz), 3.67 (1H, dq, *J* = 11.0, 7.0 Hz), 4.84 (1H, d, *J* = 10.5 Hz), 6.14 (1H, d, *J* = 10.5 Hz), 6.74 (2H, s); ^{13}C NMR ($CDCl_3$) δ 13.3 (q), 20.7 (q), 21.3 (1), 40.2 (q), 56.4 (d), 61.3 (t), 76.8 (d), 128.8 (d), 132.2 (s), 136.5 (s), 137.9 (s), 160.0 (s), 170.2 (s). HRMS Calcd for

$C_{17}H_{24}N_2O_2S$: *m/z* 320.1558. Found: *m/z* 320.1562.

cis-**18e** (R^1 = NMe_2, R^2 = Mes): Yellow oil; MS (*m/z*) 320 (M^+; 61%), 247 (M^+-CO_2Et; bp); IR (neat) 2918, 1738, 1698, 1413, 1114, 1075, 756 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (3H, t, *J* = 7.0 Hz), 2.23 (3H, s), 2.34 (6H, s), 2.99 (6H, s), 4.15 (1H, dq, *J* = 11.0, 7.0 Hz), 4.21 (1H, dq, *J* = 11.0, 7.0 Hz), 4.50 (1H, d, *J* = 8.0 Hz), 6.15 (1H, d, *J* = 8.0 Hz), 6.81 (2H, s); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 20.5 (q), 20.8 (q), 40.3 (q), 58.0 (d), 62.0 (t), 75.7 (d), 130.3 (d), 135.2 (s), 136.9 (s), 137.0 (s), 159.1 (s), 171.7 (s). HRMS Calcd for $C_{17}H_{24}N_2O_2S$: *m/z* 320.1558. Found: *m/z* 320.1558.

19e (R^1 = NMe_2, R^2 = Mes): Colorless solid, mp 116.0-119.0 °C; MS (*m/z*) 318 (M^+; 58%), 245 (M^+-CO_2Et; bp); IR (KBr) 2918, 1698, 1560, 1413, 1114, 1075, 756 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (3H, t, *J* = 7.0 Hz), 2.07 (3H, s), 2.28 (6H, s), 3.17 (6H, s), 4.08 (2H, q, *J* = 7.0 Hz), 6.86 (2H, s); ^{13}C NMR ($CDCl_3$) δ 14.1 (q), 19.8 (q), 21.2 (q), 40.1 (q), 60.1 (t), 111.8 (t), 127.9 (d), 132.8 (s), 137.3 (s), 160.4 (s), 161.7 (s), 171.5 (s). HRMS Calcd for $C_{17}H_{22}N_2O_2S$: *m/z* 318.1402. Found: *m/z* 318.1406.

19f (R^1 = NMe_2, R^2 = H): Yellow needles, mp 33.1-34.0 °C (Lit.[17a] 38.0-39.0 °C); MS (*m/z*) 201 (M^++1; bp). IR (KBr) 2925, 1724, 1630, 1353, 1164, 1086, 682 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (3H, t, *J* = 7.2 Hz), 3.16 (6H, s), 4.29 (2H, q, *J* = 7.2 Hz), 7.88 (1H, s); ^{13}C NMR ($CDCl_3$) δ 14.4 (q), 40.2 (q), 60.6 (t), 116.4 (s), 148.3 (d), 162.2 (s), 174.5 (s). HRMS Calcd for $C_8H_{12}N_2O_2S$: *m/z* 200.0619. Found: *m/z* 201.0675 (M^++1).

A Typical Procedure for the Reaction of 1,3-Thiaza-1,3-butadienes 5 with Dichlorocarbene. A hexane solution of **5e** (R^1 = NMe_2, R^2 = Mes, 92 mg, 0.39 mmol) was treated with dry $CHCl_3$ (469 mg, 10.0 mol amt.) and then with potassium *t*-butoxide (220 mg, 5.0 mol amt.) with vigorous stirring at 0 °C for 5 h. Then, the solvent was removed by evaporation from the reaction mixture, and the crude brown solid was separated by using chromatography on silica gel to obtain 5-chloro-1,3-thiazole **20e** (28 mg, 25% yield) as yellow solids.

20a (R^1 = NMe_2, R^2 = *t*-C_4H_9): Brown oil; MS (*m/z*) 220 (M^+; 33%, ^{37}Cl), 218 (M^+; 97%, ^{35}Cl), 205 (M^+-Me; 34%, ^{37}Cl), 203 (M^+-Me; bp, ^{35}Cl), 57 (*t*-C_4H_9; 41%); IR (neat) 2927, 1653, 1363, 1182, 1085, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (9H, s), 3.27 (6H, s); ^{13}C NMR ($CDCl_3$) δ = 29.8 (q), 35.6 (s), 39.5 (q), 104.0 (s), 155.3 (s) 164.9 (s). Anal. Calcd for $C_9H_{15}ClN_2S$: C, 49.42; H, 6.91; N, 12.81%. Found: C, 49.51; H, 6.80; N, 12.75%.

20e (R^1 = NMe_2, R^2 = Mes): Yellow solid, mp 125.0-128.0 °C; MS (*m/z*) 282 (M^+; 27%, ^{37}Cl), 280 (M^+; 71%, ^{35}Cl), 245 (M^+-Cl; bp), 175 (64%); IR (KBr) 2953, 1651, 1349, 1186, 1090, 682 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.14 (6H, s), 2.28 (3H, s), 3.05 (6H, s), 6.89 (2H, s); ^{13}C NMR ($CDCl_3$) δ 19.8 (q), 21.3 (q), 39.9 (q), 107.7 (s), 128.2 (d), 130.0 (s), 137.6 (s), 138.1 (s), 148.1 (s), 166.7 (s). HRMS Calcd for $C_{14}H_{17}N_2SCl$: *m/z* 280.0801. Found: *m/z* 280.0800.

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