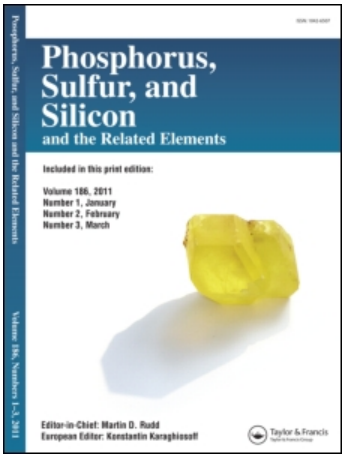

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ADDITION REACTION OF SULFUR DICHLORIDE TO FUNCTIONALIZED IMINES DIRECTED TOWARD HETEROCYCLIC SYNTHESIS

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ADDITION REACTION OF SULFUR DICHLORIDE TO FUNCTIONALIZED IMINES DIRECTED TOWARD HETEROCYCLIC SYNTHESIS

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Although it was shown that the reactions of sulfur dichloride (SCl_2) with the imines **1a–c** or with the azine **14** gave rise to very unstable 1 : 1 adducts, 1-aza- and 2-azabutadienes, **5** and **10**, reacted with SCl_2 to afford the isothiazoles **6** and the thiazoles **11**, respectively, in high yields. Addition of SCl_2 to heterocumulenes was also studied and the ketenimines **16** and diphenylketene **27** gave 1 : 1 adducts which were applied to heterocyclic synthesis as bifunctional reagents. Addition of SCl_2 to these compounds was investigated by monitoring the reactions by ^{13}C nmr spectroscopy.

INTRODUCTION

Sulfur dichloride (SCl_2) has long been known as a potential enophilic reagent which easily forms bis(2-chloroalkyl) sulfides upon addition to olefins. Such high reactivity of SCl_2 toward olefins has often been utilized in the synthesis of cyclic sulfides by treating diolefinic compounds with SCl_2.[1] If sulfur dichloride also had high affinity to carbon-heteroatom multiple bonds, it would provide a versatile entry to various heterocycles containing sulfur and other heteroatoms.

Although an enormous amount of knowledge on addition reactions of SCl_2 to carbon–carbon double bonds has been established, only a limited number of additions of SCl_2 to carbon–nitrogen multiple bonds has been reported. No reports on 1,2-addition to carbon–nitrogen double bonds seem to have been described, but SCl_2 added to sulfonyl nitriles to give 1 : 1 adducts[2] or to some cyanides and nitriles to give sulfur-containing heterocycles.[3] Another example of addition of SCl_2 to carbon-heteroatom multiple bonds is the recently reported reaction of SCl_2 with thioketones.[4]

In this paper we discuss studies of the reaction of sulfur dichloride with various imine derivatives, carried out not only to obtain fundamental knowledge of the addition behavior of the dichloride but also to apply the reactions to the synthesis of sulfur- and nitrogen-containing heterocyclic compounds. Such types of compounds have been the subject of considerable attention as candidates for physiologically active substances.

RESULTS AND DISCUSSION

Reaction with Simple Imines

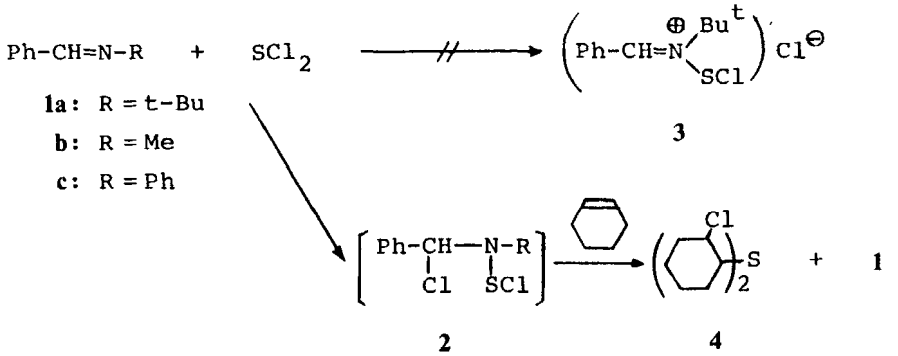
When *N*-tert-butylbenzaldimine (**1a**) was allowed to react with SCl_2 in CH_2Cl_2 at room temperature, we obtained only the hydrochloride of the imine **1a** (71%). Under the same conditions, benzylidenaniline (**1c**) also gave 61% of the hydrochloride of **1c**.

Although the origin of hydrogen chloride was attributable to chlorination of the imines by SCl_2 or to hydrolysis of an S—Cl bond, formation of imine-SCl_2 adducts was ambiguous. Hence, we followed the reaction by ^{13}C nmr spectroscopy at low temperatures and we found that direct addition of SCl_2 to the C=N bond does occur to form unstable 1 : 1 adducts.

The spectrum shown in Figure 1B was taken soon after the mixing of 1 equiv of SCl_2 with the imine **1a** in $CDCl_3$ at $-70°C$. The signals of **1a** shown in Figure 1A were immediately displaced by a new spectrum which featured a new sp^3 carbon signal at 80 ppm (Figure 1B). The result suggested formation of the 1,2-addition product **2a**. Since it is reported that SCl_2 forms a 1 : 2 salt with pyridine and a 1 : 1 salt with α-picoline,[5] formation of the iminium salt **3a** was another possibility. Such a type of salt which preserves the carbon-heteroatom double bond was also assumed in the reaction with thiobenzophenone.[4] However, the formation of the salt **3a** was simply excluded by the disappearance of the imine carbon signal in Figure 1B. When the temperature was gradually elevated, the adduct **2a** proved to be stable up to $-10°C$, but started to change at higher temperatures. The spectrum taken after 2 days at 25°C showed exclusive formation of the hydrochloride of **1a** (Figure 1D).

Monitoring of the reactions of the imines **1b** and **1c** with SCl_2 by ^{13}C nmr also confirmed the immediate disappearance of the imine **1** and appearance of a new sp^3 carbon signal at 84.0 ppm (R = Ph) or at 90.0 ppm (R = Me), which was in accord with the formation of the 1 : 1 adduct **2**.

It was found that the adduct **2** easily loses SCl_2 and, hence, our attempts to trap this unstable adduct using various reagents were unsuccessful. For example, addition of 2 equiv of cyclohexene to a solution of **2a** in $CDCl_3$ at $-70°C$ caused no reaction, but the ^{13}C spectrum slowly changed at above $-10°C$. The products



SCHEME 1

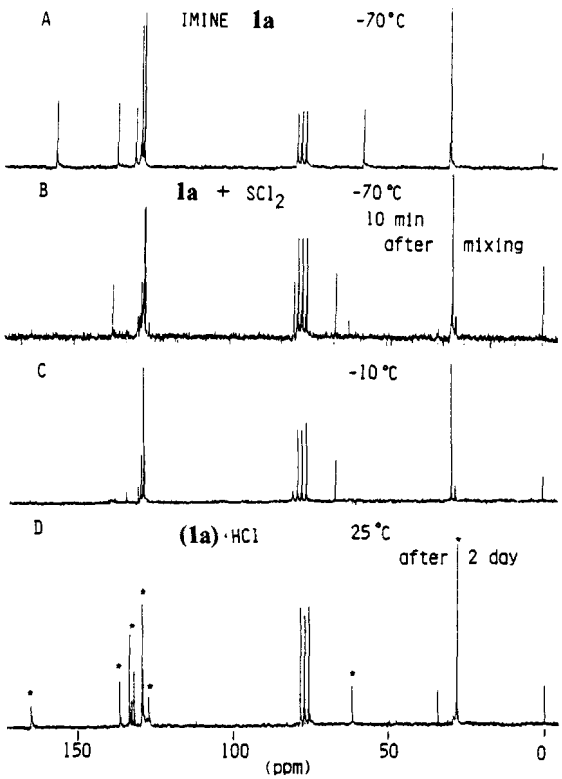


FIGURE 1 Monitoring of the reaction of the imine **1a** with SCl_2.

obtained after standing for 1 day at 25°C were bis(2-chlorocyclohexyl) sulfide (**4**) and the starting imine **1a**. The 1 : 1 adducts **2b** and **2c** also gave similar results.

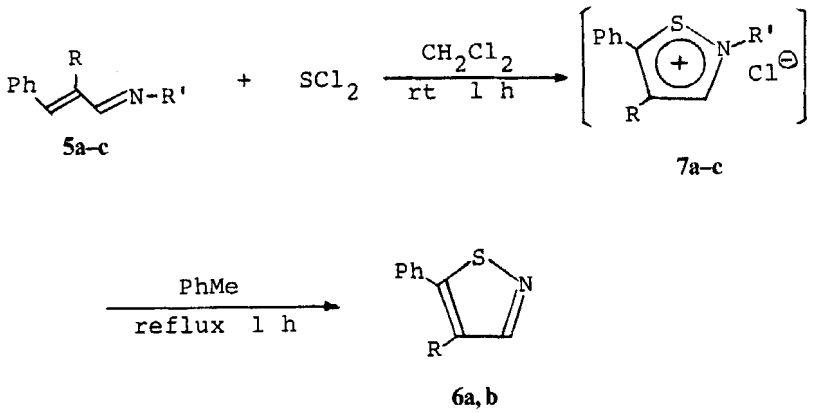
On the other hand, an imine derived from an aliphatic aldehyde, *N*-tert-butylpropanimine, reacted with SCl_2 to form only a complex mixture of products. This is probably because of equilibrium between the imine and an enamine which is known to react with SCl_2.[6] In this case, addition of cyclohexene did not give rise to SCl_2 extrusion.

Reaction with Conjugated Imines

Since it was found that sulfur dichloride is highly reactive toward a C=N bond, it is of interest to discuss the addition behavior of SCl_2 to 1- or 2-azabutadiene derivatives which contain an alkenyl group conjugated to an imino function. The reaction of SCl_2 with conjugated dienes such as butadiene and cyclopentadiene derivatives usually gave polymers[7] and the formation of thiophene derivatives in very low yields was reported in a few cases.[8,9]

A. Reaction with 1-Azadienes

1-*t*-Butyl-4-phenyl-1-aza-1,3-butadiene (**5a**) was allowed to react with 0.5 equiv of SCl_2 in CH_2Cl_2 at room temperature for 1 h. The nmr spectrum of the reaction



SCHEME 2

mixture suggested quantitative formation of the isothiazolium salt **7a** (*vide infra*). Isolation of **7a** was not easy. The solvent was removed and the residue was heated in toluene for 1 h to give 5-phenylisothiazole (**6a**) in 86% yield as a result of de-*tert*-butylation of **7a**.

An equimolar reaction of the azadiene **5a** with SCl_2 caused an unexpected decrease in the yield of the isothiazole **6a**. As the role of excess azadiene **5** was considered to be that of a dehydrochlorinating agent, an equimolar reaction was performed in the presence of a base such as Et_3N, PhCH=N—Me, or powdered potassium carbonate. However, the yield of the isothiazole did not improve (see Table I). In a few runs, 4-chloro-5-phenylisothiazole (**8**) was obtained as a by-product.

TABLE I

Formation of the isothiazoles **6** from 1-azadienes **5** and SCl_2

1-Azadiene **5**		Base	Mole ratio SCl_2/**5**	Yield of **6** (%)
R	R′			
H	*t*-Bu	—	0.5	86
H	*t*-Bu	—	1.0	34[c,d,e]
H	*t*-Bu	Et_3N[a]	1.0	57
H	*t*-Bu	PhCH=NMe[a]	1.0	24[c,f]
H	*t*-Bu	K_2CO_3[b]	1.0	30
Me	*t*-Bu	—	0.5	91
Me	*t*-Bu	Et_3N[a]	1.0	32
Me	*i*-Pr	—	1.0	57[g,h]

[a] 1 equiv.
[b] 3 equiv.
[c] Determined by GLC.
[d] Refluxed for 5 h in toluene.
[e] 4-Chloro-5-phenylisothiazole (**8**) was obtained in 5% yield.
[f] The isothiazole **8** was obtained in 3% yield.
[g] Determined by nmr.
[h] Refluxed for 15 h in toluene.

The azadienes **5b** (R = Me, R′ = *t*-Bu) and **5c** (R = Me, R′ = *i*-Pr) also gave the corresponding isothiazole **6b** and these results are also listed in Table I. Under the conditions employed herein, thermal dealkylation of the *N*-isopropyl isothiazolium salt **7** (R = Me, R′ = *i*-Pr) was very slow and the *N*-methyl derivative (R = H, R′ = Me) gave no isothiazole even when it was refluxed in toluene for 5 h. Furthermore, the *N*-phenyl-1-azadiene (R = H, R′ = Ph) afforded neither the salt **7** nor the isothiazole **6a**.

To clarify the reaction paths, we again followed the reaction by ^{13}C nmr. The spectrum of a mixture of the 1-azadiene **5a** and SCl_2 (0.5 equiv) observed soon after the mixing at −50°C (Figure 2B) showed immediate disappearance of **5a** (Figure 2A). If direct addition of SCl_2 to C=C and/or C=N bonds had occurred, an sp^3 carbon signal (or signals) would be observed. However, no new sp^3 carbon formation was observed and the spectrum showed two signals at 164 and 168 ppm, assignable to imino carbons, and two sets of *t*-Bu signals, which were shifted to lower fields. Thus, we assumed that formation of a 2 : 1 salt of **5a** and SCl_2 was more favorable than formation of a 1 : 1 salt in the initial step, analogous to the reported 2 : 1 salt of pyridine and SCl_2.[5] Electrophilic addition of SCl_2 across the C=C bond must have been suppressed by electron withdrawal of the imino group.

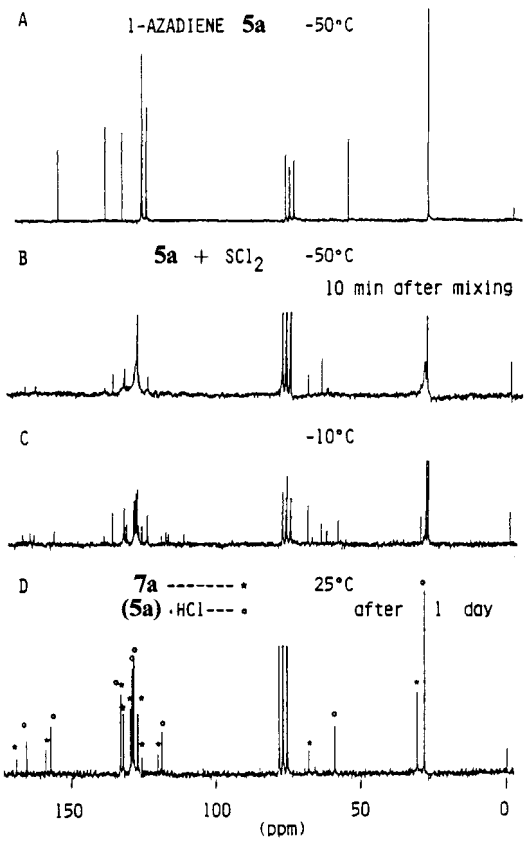
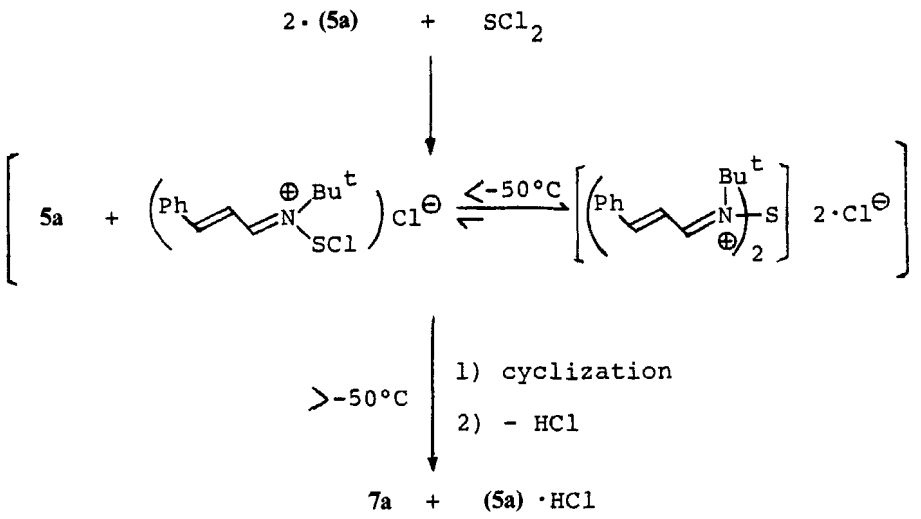


FIGURE 2 Monitoring of the reaction of the 1-azadiene **5a** with SCl_2.



SCHEME 3

Although the 2 : 1 salt was stable up to −50°C, the spectrum gradually changed with rise in temperature (Figure 2C) and finally, at 25°C, it showed complete agreement with those of the isothiazolium salt **7a** and hydrochloride of **5a** (Figure 2D).

The isothiazolium salt **7a** seems to be formed through the 1 : 1 salt which is in equilibrium with the 2 : 1 salt as shown in Scheme 3. This is consistent with the fact that two moles of the azadiene is indispensable for the present reaction. When the reaction was carried out using 2 equiv of SCl_2, on the other hand, no isothiazole **6a** but a complex mixture of products was obtained.

From the mixture, 4-chloro-5-phenylisothiazole (**8**, 9%) and 3-chloro-2-formylbenzothiophene (**9**, 7%)[10] (which implied addition of SCl_2 to the C=C bond) were isolated. Furthermore, dichloro- and trichlorocinnamaldehydes formed by hydrolysis of the corresponding chlorinated azadienes were also detected. Thus, excessive amounts of SCl_2 make the reaction more complex by halogenation of the azadiene and by addition of SCl_2 to the C=C bond. Formation of the isothiazole **6a** by thermal debutylation of the isothiazolium salt **7a** was unambiguously proved by heating a pure sample of **7a**, which resulted in elimination of the *t*-Bu group as *t*-BuCl.

$$\mathbf{7a} \xrightarrow[120°C,\ 0.5\ h]{\Delta/CDCl_3} \underset{(92\%)}{\mathbf{6a}} + \underset{(76\%)}{{}^tBuCl} + \underset{(13\%)}{Me_2C{=}CH_2}$$

As SCl_2 is known to be in equilibrium with sulfur monochloride (S_2Cl_2), it was possible that the latter was the active species in this reaction. But the reaction of **5a** with S_2Cl_2 (0.5 equiv) under the same conditions gave neither isothiazolium salt nor the isothiazole.

TABLE II

Formation of the thiazoles **11** from 2-azadienes **10** and SCl_2

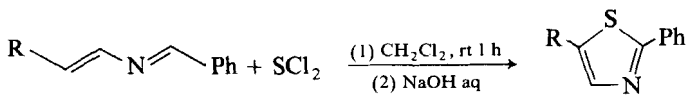
2-Azadiene **10** R	Mole ratio SCl_2/**10**	Yield of **11**[a] (%)
Ph	1.0	**11a** 85 (93)
Ph	2.0	**11a** 78
i-Pr	1.0	**11b** 70 (84)
i-Pr	3.0	**11b** —[b](83)

[a]Yields in parentheses are those determined by ^1H nmr.
[b]Not isolated.

B. Reaction with 2-Azadienes

The effect of changing the conjugated azabutadiene system by shifting the nitrogen atom from the 1- to the 2-position was then studied.

1,4-Diphenyl-2-aza-1,3-butadiene (**10a**) was allowed to react with SCl_2 in CH_2Cl_2 at room temperature for 1 h to give the hydrochloride of the thiazole **11a** quantitatively (by nmr). The reaction mixture was treated with an alkaline solution and chromatographed to afford 2,5-diphenylthiazole (**11a**) in 85% yield. Similarly, the 2-azadiene **10b** gave the corresponding thiazole **11b** in 70% yield.



10a,b **11a,b**

Contrary to the reaction with the 1-azadienes, the reaction proceeded with 1 equiv of SCl_2. Hence, the path of the present reaction cannot be considered to include the formation of a 2 : 1 salt which was the case with the 1-azadienes. Monitoring of the reaction by ^{13}C nmr readily explained the different addition pattern of SCl_2. The spectrum taken soon after the mixing of SCl_2 with the 2-azadiene **10a** at $-52°C$ (Figure 3B) revealed immediate disappearance of the signals due to **10a**. However, four sp^3 carbon signals and an imino carbon signal were observed. This phenomenon is quite different from that of the reaction with the 1-azadiene **5a** (see Figure 2B). The spectrum implied direct addition of SCl_2 to the C=C bond of **10a** forming the unstable adduct **12**.

Existence of four sp^3 carbon signals is considered to correspond to two isomers of **12a**, although one of the imino carbon signals was not clear in the spectrum, probably because of limited signal accumulation. Since the C=C bond is not as electron deficient as those in the 1-azadienes, electrophilic addition of SCl_2 to the C=C bond must have been predominant.

The adduct **12a** seemed rather unstable, the spectrum gradually changed even at $-52°C$, and the appearance of the hydrochloride of the thiazole **11a** was observed. After the temperature was raised up to 0°C, the spectrum of the mixture showed good agreement with that of the hydrochloride of **11a** (Figure 3D).

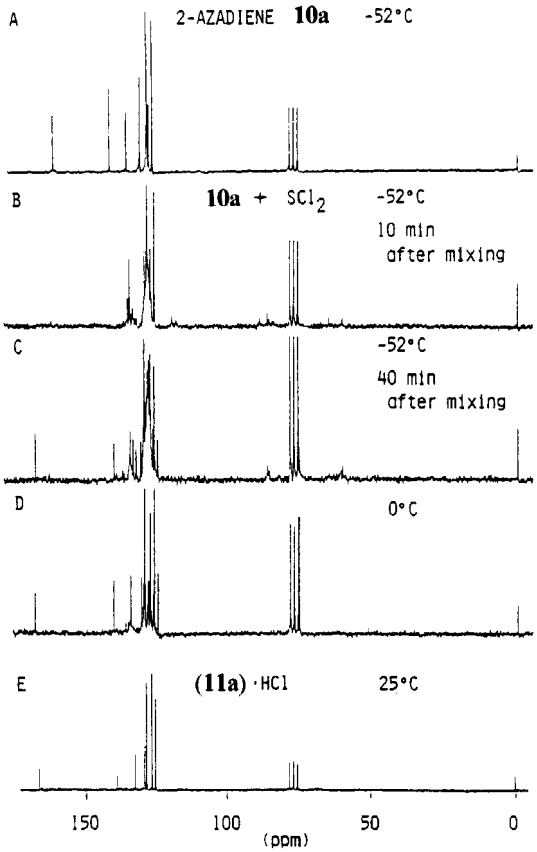
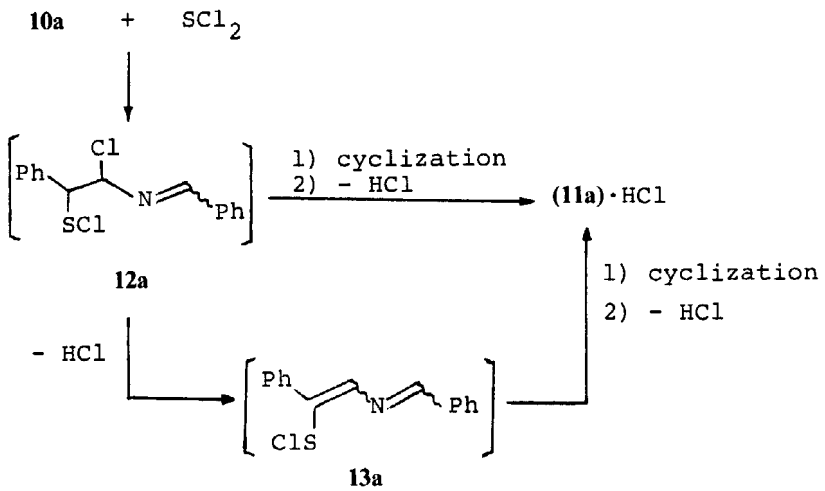


FIGURE 3 Monitoring of the reaction of the 2-azadiene **10a** with SCl_2.



SCHEME 4

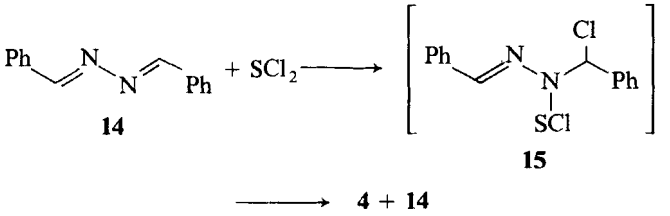
The reaction probably proceeded via cyclization of **12a** followed by dehydrochlorination to form the thiazole ring. However, the intermediacy of 4-chlorosulfenyl-2-azadiene **13a**, which would be generated by dehydrochlorination of **12a**, cannot be excluded.

C. Reaction with an Azine

Since heterocyclic compounds were obtained in good yields from SCl_2 and conjugated azadienes, the reaction of SCl_2 with an azine, which in a sense is a diazabutadiene, was investigated.

When benzaldazine (**14**) was treated with SCl_2 similarly to the reaction of the 2-azadienes, the anticipated heterocycle, 2,5-diphenyl-1,3,4-thiadiazole, was not obtained. The ^1H nmr spectrum implied the formation of an adduct, but all efforts to isolate it were in vain. The starting azine was always recovered after work-up.

Monitoring of the reaction of SCl_2 with the azine **14** by ^{13}C nmr showed the addition behavior of SCl_2 to **14** was almost the same as that with simple imines. The spectrum taken soon after the mixing at $-70°C$ showed the appearance of an sp^3 carbon signal at 87.0 ppm and a new imino carbon signal at 150.1 ppm which is consistent with addition of SCl_2 to one of the C=N bonds. Addition of cyclohexene to the adduct **15** at $-70°C$ caused a slight change in the signals and formation of bis(2-chlorocyclohexyl) sulfide (**4**) was detected. Finally, the spectrum showed quantitative recovery of **14** and formation of **4**.



14 **15**

⟶ **4** + **14**

Reaction with Heterocumulenes

Heterocumulenes containing at least one carbon–nitrogen double bond were treated with SCl_2.

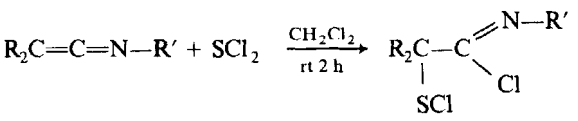
N-phenyldiphenylketenimine (**16a**) reacted with SCl_2 at room temperature to give 2-chlorosulfenyl-2,2-diphenylacetimidoyl chloride (**17a**) quantitatively. Formation

TABLE III

Formation of the imidoyl chloride **17** from ketenimines **16** and SCl_2

Imidoyl chloride **17**		Yield
R	R′	(%)
Ph	Ph	100
Ph	*p*-tolyl	97
Me	Ph	92
Me	*p*-tolyl	93

of the α-chlorosulfenylimidoyl chloride **17** is a result of exclusive addition of SCl_2 to the C=C bond of the cumulated system.

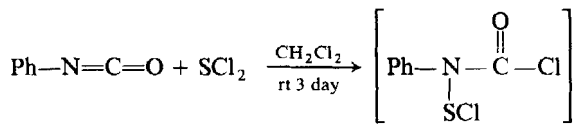


16a–d **17a–d**

On the other hand, heterocumulenes with two carbon–heteroatom double bonds did not give stable 1 : 1 adducts.

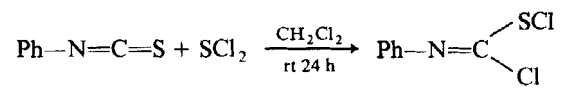
N,N-diphenylcarbodiimide (**18**) reacted with SCl_2 at room temperature to give a polymeric product. The ^{13}C nmr signals of the carbodiimide **18** disappeared immediately after mixing with SCl_2 at −50°C and formation of a 1 : 1 adduct was suggested. The ir spectrum also supported the addition of SCl_2 by showing a strong absorption band at 1650 cm^{-1}. The adduct was stable up to 0°C, but the spectrum turned complex when the mixture was allowed to stand at room temperature. When cyclohexene was added to the reaction mixture at 0°C, the sulfide **4** was obtained in 65% yield along with the starting carbodiimide.

In the case of the reaction of phenyl isocyanate (**19**) with SCl_2 (3 equiv), a strong absorption band at 1765 cm^{-1} (which indicated formation of the 1 : 1 adduct **20**) gradually increased in the ir spectrum. After 3 days, the reaction mixture was distilled to give only the isocyanate **19** (77%) which showed the thermal instability of the 1 : 1 adduct.



19 **20**

Phenyl isothiocyanate (**21**) was less reactive than the preceding heterocumlenes and no change was observed in the ir spectrum after two days when equimolar amounts of **21** and SCl_2 reacted at room temperature. By using 3 equiv of SCl_2, the chlorinated isothiocyanate **22** was isolated quantitatively. The chlorination was presumably caused by chlorine liberated from SCl_2 according to the known equilibrium with S_2Cl_2.

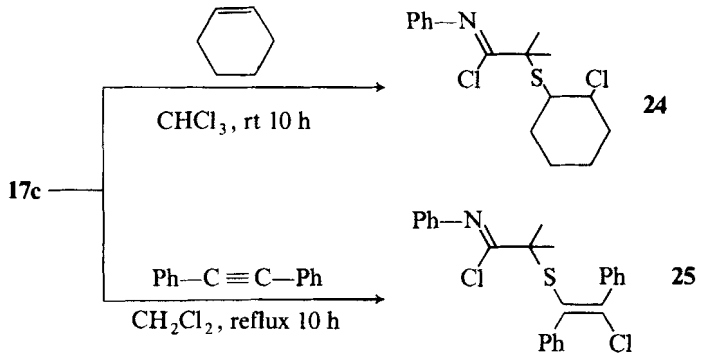


21 **22**

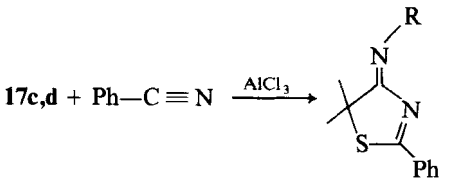
Reaction of the Ketenimine–SCl_2 adduct 17

The ketenimine–SCl_2 adduct **17** is expected to be quite useful because of its bifunctionality arising from the chloroimidoyl group and the chlorosulfenyl group. The chlorosulfenyl group is reactive toward olefinic and acetylenic compounds. For

example, the adduct **17c** reacted with cyclohexene to give the adduct **24** quantitatively. It also added to diphenylacetylene to afford the 1 : 1 adduct **25** in 73% yield.

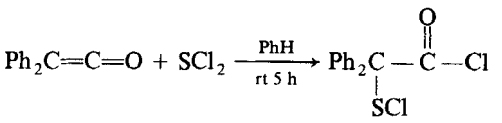


When the adduct **17d** was treated with benzonitrile in the presence of aluminum chloride at 100°C for 10 h, the sulfur-containing heterocycle, 4-imino-1,3-thiazoline, **26d** was formed in 23% yield. The adduct **17c** also gave the corresponding thiazoline **26c** when treated with an equimolar amount of benzonitrile in refluxing CH_2Cl_2 in the presence of aluminum chloride (13%).

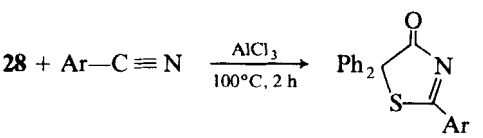


26c: R = Ph
d: R = *p*-tolyl

The same type of reaction was found for the diphenylketene–SCl_2 adduct **28**, which was obtained quantitatively by treating the ketene **27** with SCl_2 in benzene at room temperature. When the α-chlorosulfenyl acid chloride **28** reacted with aryl nitriles in the presence of aluminum chloride, thiazolones **29** were obtained.

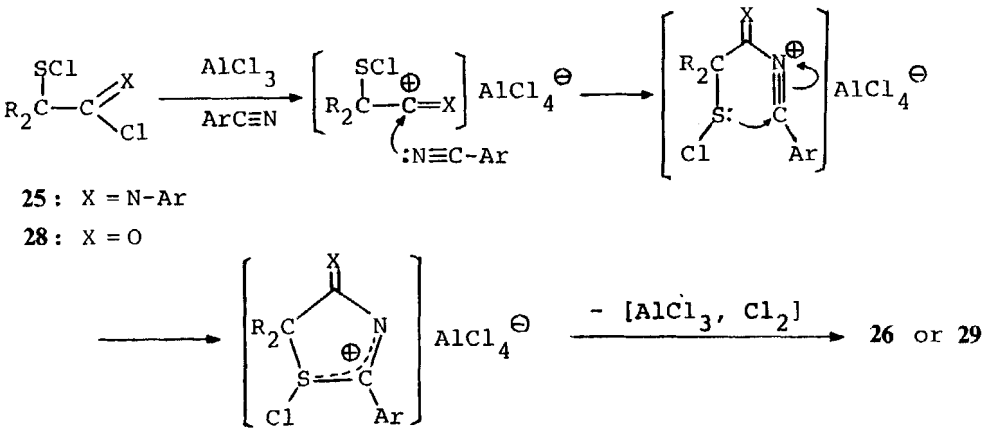


27 **28**



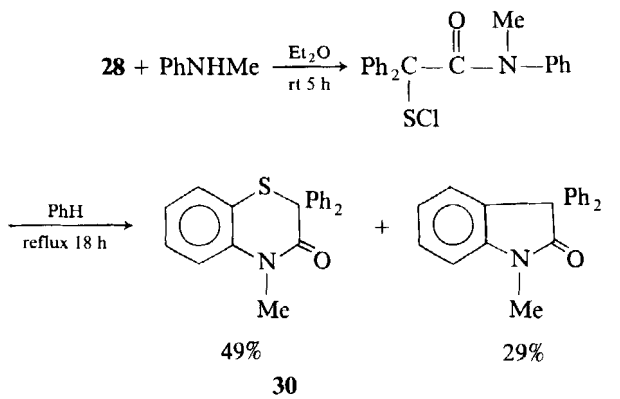
29a: Ar = Ph (13%)
b: Ar = *p*-tolyl (13%)

The formation of the iminothiazoline **26** and the thiazolone **29** is explained by the mechanism depicted in the following scheme.



SCHEME 5

Another example of the utility of the adduct **28** is the following reaction to form a benzothiazine derivative **30**. Similar treatment of the ketenimine—SCl_2 adduct **17**, however, did not give rise to the corresponding benzothiazine derivative.



30

EXPERIMENTAL

Melting points were determined with a Yanagimoto micromelting point apparatus and melting and boiling points are uncorrected. The nmr spectra were obtained on JEOL JNM PMX 60 and JEOL JNM FX 90Q FT spectrometers in $CDCl_3$ solutions with tetramethylsilane as an internal standard. The ir spectra were recorded with a JASCO IRA-1 spectrometer. The mass spectra were taken with a Hitachi RMU-6E spectrometer at an ionizing voltage of 70 eV.

All the reactions were done under a nitrogen atmosphere and distillations were carried out by the bulb-to-bulb method.

Materials. Commercially available reagents were used unless otherwise noted. Sulfur dichloride was prepared by passing chlorine through S_2Cl_2 containing 2 mol% of tin chloride and distilled (bp 59–63°C). The imines **1**, the 1-azadienes **5**, 2-azadienes **10**, the azine **14**, and the heterocumulenes **16**, **18**, and **27** were prepared by known methods.

Monitoring of Reactions by ^{13}C nmr. A 10 mm ϕ nmr tube containing a solution of the imine **1a** (322 mg, 2.0 mmol) in $CDCl_3$ (2.0 ml) was placed in a spectrometer probe (90Q) cooled to −70°C by a variable-temperature controller using liquid nitrogen as a coolant. Satisfactory spectra were obtained by 100-fold accumulation (200 times in some cases) which required about 8 min. After the measurement, the tube was dipped in liquid nitrogen and a solution of SCl_2 (206 mg, 2.0 mmol) in $CDCl_3$ (0.5 ml) was injected through a rubber septum cap covering the tube. The solidified mixture was again inserted into the probe cooled to −70°C and the mixture slowly liquefied in several minutes at which point measurements were started to monitor the reaction. The spectra were taken several times at −70, −50, −30, −10, 0, and 25°C and every temperature was maintained for 1 h when there was no significant change in the spectrum. Monitoring of other runs was performed in the same manner.

Reaction of the Imine **1** *with* SCl_2. To a solution of *N-tert*-butylbenzaldimine (**1a**, 483 mg, 3.0 mmol) in CH_2Cl_2 (20 ml) was added dropwise SCl_2 (618 mg, 6.0 mmol) in CH_2Cl_2 (10 ml) and the mixture was stirred for 1 h at room temperature. The solvent was removed *in vacuo* and the residue was triturated with ether to give 335 mg (56%) of the hydrochloride of **1a**. Similarly, benzylidenaniline (**1c**, 3.0 mmol) and SCl_2 (3.0 mmol) gave 400 mg (61%) of the hydrochloride of **1c**. No chlorination was observed for the imines recovered as the hydrochlorides by spectral analysis.

Reaction of the Adducts **2** *with Cyclohexene.* The reaction of the adducts **2a–c** generated *in situ* with cyclohexene to give bis(2-chlorocyclohexyl) sulfide (**4**) and the starting imine **1** was monitored by ^{13}C nmr. The reaction was also done in a flask. To a solution of the imine **1a** (805 mg, 5.0 mmol) in CH_2Cl_2 (10 ml) was added SCl_2 (515 mg, 5.0 mmol) in CH_2Cl_2 (10 ml) with stirring at −78°C and the temperature was gradually elevated to −30°C. Then cyclohexene (820 mg, 10 mmol) was added to the mixture at −30°C and, after 1 h, the mixture was allowed to stand at room temperature for 1 day to give **4** (62%) and **1a** (78%); yields were determined by GLC.

Reaction with 1-Azabutadienes **5**. To a solution of 1-*tert*-butyl-4-phenyl-1-aza-1,3-butadiene (**5a**, 553 mg, 2.96 mmol) in CH_2Cl_2 (20 ml) was added dropwise SCl_2 (152 mg, 1.5 mmol) in CH_2Cl_2 (10 ml) at 0°C and the mixture was stirred for 1 h at room temperature. After concentration *in vacuo* without heating, toluene (10 ml) was added to the residue and refluxed for 1 h. The toluene-insoluble part was washed with benzene and the combined solution was concentrated, and chromatographed (on SiO_2-elution by a 1 : 1 mixture of benzene and hexane) to give 204 mg (86%) of 5-phenylisothiazole (**6a**). From the benzene-insoluble residue (394 mg), the hydrochloride of **1a** was obtained quantitatively.

The isothiazole **6a**: bp 80°C (0.3 mmHg); mp 50–51°C (colorless granules); ^1H nmr (δ) 7.2–7.7 (m, 6 H, aromatic H and 4-H), 8.37 (d, J = 1.8 Hz, 1 H, 3-H); ^{13}C nmr (ppm) 119.6 (d), 126.5 (d), 128.9 (d), 129.3 (d), 130.6 (s), 158.0 (d), 167.1 (s); mass spectrum m/e 161 (M^+). Anal. Calcd for C_9H_7NS: C, 67.05; H, 4.38; N, 8.69; S, 19.89. Found: C, 66.51; H, 4.34; N, 8.42; S, 19.63.

When 24 mmol of SCl_2 reacted with 12 mmol of **5a** under the same conditions, 3.0 g of oily material was obtained. A part (1.7 g) of the oil was heated in refluxing toluene (5 ml) for 5 h and chromatographed (on SiO_2-eluted by a 1 : 1 mixture of benzene–hexane) to give 120 mg (9%) of 4-chloro-5-phenylisothiazole (**8**) and 94 mg (7%) of 3-chloro-2-formylbenzothiophene (**9**) along with **5a** (14%), cinnamaldehyde (18%), dichlorinated (12%) and trichlorinated cinnamaldehyde (18%). The aldehydes were characterized by ir and mass spectra.

The isothiazole **8** (pale yellow liquid): bp 129–130°C (1 mmHg); ^1H nmr (δ) 7.28–7.77 (m, 5 H, Ph), 8.28 (s, 1 H, 3-H); ^{13}C nmr (ppm) 128.2 (d), 128.8 (s), 129.0 (d), 129.8 (d), 157.5 (d), 159.0 (s); mass spectrum m/e 195 (M^+). Anal. Calcd for C_9H_6ClNS: C, 55.25; H, 3.09; N, 7.16; S, 16.38. Found: C, 55.04; H, 3.26; N, 6.93; S, 15.58.

The benzothiophene **9**: mp 112–113°C (colorless columns from hexane); ir (KBr disk) 1650 cm^{-1} (C=O); ^1H nmr (δ) 7.38–8.08 (m, 4 H, aromatic H), 10.28 (s, 1 H, CHO); ^{13}C nmr (ppm) 106.6 (d), 123.5 (d), 123.8 (d), 125.8 (d), 129.3 (s), 135.3 (s), 136.6 (s), 140.3 (s), 183.2 (d); mass spectrum m/e 196 (M^+). Anal. Calcd for C_9H_5ClOS: C, 54.97; H, 2.56; Cl, 18.03; S, 16.30. Found: C, 54.70; H, 2.76; Cl, 18.23; S, 16.04.

Similarly, 360 mg (91%) of 4-methyl-5-phenylisothiazole (**6b**) was obtained from 915 mg (4.55 mmol) of the 1-azadiene **5b** and 234 mg (2.25 mmol) of SCl_2.

The isothiazole **6b** (colorless oil): bp 95°C (3 mmHg); ^1H nmr (δ) 2.23 (s, 3 H, Me), 7.13–7.57 (m, 5 H, Ph), 8.00 (s, 1 H, 3-H); ^{13}C nmr (ppm) 11.5 (q), 127.8 (s), 128.2 (d), 128.7 (d), 129.3 (d), 130.9 (s), 160.0 (d), 160.7 (s); mass spectrum m/e 175 (M^+).

The Isothiazolium Chloride **7a**. After the reaction was carried out in a similar manner to the preceding run employing 1.122 g (6.0 mmol) of **5a** and 309 mg (3.0 mmol) of SCl_2, the solvent was removed *in vacuo* without heating. An oily residue was dissolved in dry acetone (30 ml) and was allowed to stand in a refrigerator for 2 days to afford 545 mg of a mixture of **7a** and hydrochloride of **5a** as a crystalline solid.

The crystals were washed with dry acetone several times and 145 mg (20%) of the salt **7a** precipitated from the acetone solution after 3 days: (colorless needles): ^{1}H nmr (δ) 1.99 (s, 9 H, *t*-Bu), 7.4–7.8 (m, 5 H, Ph), 8.11 (d, J = 2.9 Hz, 1 H, 4-H), 10.90 (d, J = 2.9 Hz, 1 H, 3-H); ^{13}C nmr (ppm) 31.2 (q), 68.6 (s), 121.8 (d), 126.6 (s), 127.7 (d), 130.3 (d), 133.6 (d), 161.5 (d), 168.7 (s).

Reactions with 2-Azadienes. To a solution of 560 mg (2.7 mmol) of 1,4-diphenyl-2-aza-1,3-butadiene (**10a**) in CH_2Cl_2 was added dropwise SCl_2 (278 mg, 2.7 mmol) in CH_2Cl_2 (10 ml) at 0°C and the mixture was stirred for 1 h. The resulting mixture was washed (*aq* NaOH), extracted (CH_2Cl_2), dried (Na_2SO_4), and chromatographed (on SiO_2–with benzene) to afford 542 mg (85%) of 2,5-diphenylthiazole (**11a**): mp 105–106°C (colorless plates from hexane); ^{1}H nmr (δ) 7.10–7.67 (m, 8 H), 7.74–8.10 (m, 3 H); ^{13}C nmr (ppm) 126.3 (d), 126.5 (d), 128.1 (d), 128.8 (d), 129.0 (d), 129.8 (d), 131.3 (s), 133.7 (s), 139.1 (s and d), 167.0 (s); mass spectrum m/e 237 (M^+). Anal. Calcd for $C_{15}H_{11}NS$: C, 75.92; H, 4.67; N, 5.90; S, 13.51. Found: C, 75.64; H, 4.66; N, 5.93; S, 13.47.

Similarly, 5-isopropyl-2-phenylthiazole (**11b**) was obtained in 70% yield starting from 546 mg (5.3 mmol) of the 2-azadiene **10b** and 843 mg (5.3 mmol) of SCl_2: (colorless oil): bp 85°C (0.15 mmHg); ^{1}H nmr (δ) 1.40 (d, 6 H, 2 Me), 3.23 (sept, 1 H, CH), 7.20–7.53 (m, 4 H, 3 protons of Ph and 4-H), 7.7–8.0 (m, 2 H, 2 protons of Ph); ^{13}C nmr (ppm) 24.7, 28.0, 126.2, 128.9, 129.5, 134.1, 138.5, 147.6, 166.0; mass spectrum m/e 203 (M^+).

Reaction with the Ketenimines **16**. To a solution of SCl_2 (620 mg, 6.0 mmol) in CH_2Cl_2 (30 ml) was added a solution of *N*-phenyldiphenylketenimine (**16a**, 1.35 g, 5.0 mmol) in CH_2Cl_2 (20 ml) and the mixture was stirred for 2 h at room temperature. The ir spectrum of the mixture showed disappearance of the characteristic absorption of **16a** at 1990 cm^{-1} and appearance of a strong absorption band at 1665 cm^{-1}. The solvent was removed *in vacuo* to give 1.86 g (100%) of yellow solid of *N*-phenyl-2,2-diphenyl-2-chlorosulfenylacetimidoyl chloride (**17a**), which was recrystallized from benzene–hexane to give yellow columns: mp 118–120°C; ir (Nujol) 1665 cm^{-1} (C=N); ^{1}H nmr (δ) 6.9–7.9 (aromatic H); ^{13}C nmr (ppm) 77.3, 121.0, 126.5, 128.1, 128.5, 129.0, 130.4, 136.4, 144.2, 147.6; mass spectrum m/e 371 (M^+). Anal. Calcd for $C_{20}H_{15}Cl_2NS$: C, 64.52; H, 4.06; Cl 19.04; N, 3.76; S, 8.61. Found: C, 64.67; H, 3.85; Cl, 18.93; N, 3.75; S, 8.53.

The imidoyl chlorides **17b–d** were obtained similarly. **17b**: mp 122–125°C (yellow columns from benzene–hexane); ir (Nujol) 1660 cm^{-1} (C=N); ^{1}H nmr (δ) 2.30 (s, 3 H, Me); 7.0–7.9 (m, 14 H, aromatic H); mass spectrum m/e 385 (M^+). Anal. Calcd for $C_{21}H_{17}Cl_2NS$: C, 65.29; H, 4.44; Cl, 18.35; N, 3.63; S, 8.30. Found: C, 65.37; H, 4.27; Cl, 18.15; N, 3.69; S, 8.42. **17c**: bp 107°C (0.07 mmHg); ir (neat) 1670 cm^{-1} (C=N); ^{1}H nmr (δ) 1.82 (s, 6 H, 2 Me), 6.8–7.6 (m, 5 H, Ph); ^{13}C nmr (ppm) 25.2, 60.8, 120.4, 125.6, 128.8, 145.6, 148.3; mass spectrum m/e 247 (M^+). **17d**: mp 43–45°C; ir (Nujol) 1665 cm^{-1} (C=N); ^{1}H nmr (δ) 1.80 (s, 6 H, Me), 2.31 (s, 3 H, Me), 6.7–7.3 (m, 4 H, aromatic H); ^{13}C nmr (ppm) 20.9, 25.2, 60.8, 120.0, 120.6, 129.4, 135.5, 142.8; mass spectrum m/e 261 (M^+).

Reaction with Phenyl Isothiocyanate **21**. To a solution of **21** (2.70 g, 20.0 mmol) in CH_2Cl_2 (30 ml) was added SCl_2 (6.18 g, 60 mmol) in CH_2Cl_2 (20 ml) at 0°C and the mixture was stirred for 24 h at room temperature. Distillation of the resulting mixture gave 2.00 g (96%) of *N*-phenylchlorosulfenylformimidoyl chloride (**22**) as a yellow liquid: bp 65–70°C (0.07 mmHg); ir (neat) 1665 cm^{-1} (C=N); ^{1}H nmr (δ) 6.5–7.7 (m, aromatic H); ^{13}C nmr (ppm) 125.5 (d), 125.8 (d), 128.9 (d), 135.1 (s), 144.5 (s); mass spectrum m/e 169 (M^+). The ir spectrum of **22** showed agreement with that of an authentic sample prepared from **21** and chlorine.

Reaction of the Ketenimine–SCl_2 Adduct **17**. To a well stirred mixture of $AlCl_3$ (0.74 g, 5.5 mmol) and benzonitrile (4.15 g, 40 mmol) was added the adduct **17d** (1.31 g, 5.0 mmol) in the nitrile (4.15 g) and the mixture was stirred for 10 h at 100°C. The resulting mixture was extracted (ether-1*N* NaOH), dried (Na_2SO_4), and was distilled to remove the excess nitrile. The residue was chromatographed to give 320 mg (23%) of 5,5-dimethyl-2-phenyl-4-*p*-tolylimino-1,3-thiazoline (**26d**) which was recrystallized from hexane to give yellow needles: mp 93–94°C; ir (KBr disk) 1640 cm^{-1} (C=N); ^{1}H nmr (δ) 1.87 (s, 6 H, 2 Me), 2.40 (s, 3 H, Me), 7.0–8.1 (m, 9 H, aromatic H); ^{13}C nmr (ppm) 20.9 (q), 29.7 (q), 60.4 (s), 123.2 (s), 128.6 (d), 128.8 (d), 133.6 (d), 140.0 (d), 174.9 (s), 181.2 (s); mass spectrum m/e 294 (M^+). Anal. Calcd for $C_{18}H_{18}N_2S$: C, 73.21; H, 6.20; N, 9.37; S, 10.72. Found: C, 73.43; H, 6.16; N, 9.52; S, 10.89.

Similarly 5,5-dimethyl-2-phenyl-4-phenylimino-1,3-thiazoline **26c** was obtained in 13% yield when 1.24 g (5.0 mmol) of **17c** and 0.62 g (6.0 mmol) of benzonitrile were refluxed in CH_2Cl_2 for 5 h in the presence of 0.80 g (6.0 mmol) of $AlCl_3$: mp 121–122°C (yellow needles from hexane); ir (Nujol) 1680 and 1640 cm^{-1} (C=N); ^{1}H nmr (δ) 1.81 (s, 6 H, 2 Me), 7.1–7.6 (m, 8 H), 7.9–8.0 (m, 2 H); mass spectrum m/e 280 (M^+).

The Diphenylketene–SCl_2 Adduct **28**. To a solution of the ketene **27** (9.80 g, 50.5 mmol) in benzene (40 ml) was added SCl_2 (5.49 g, 53.3 mmol) in benzene (10 ml) and was allowed to react for 5 h at room

temperature. Removal of the solvent gave 14.87 g (99%) of 1-chlorosulfenyldiphenylacetyl chloride (**28**) as yellow plates: mp 94–96°C (from benzene); ir (Nujol) 1760 cm^{-1} (C=O); ^1H nmr (δ) 7.1–7.6 (m); ^{13}C nmr (ppm) 79.7 (s), 128.7 (d), 129.5 (d), 134.7 (s), 172.1 (s); mass spectrum *m/e* 296 (M^+). Anal. Calcd for $C_{14}H_{10}Cl_2OS$: C, 56.57; H, 3.37; Cl, 23.91; S, 10.77. Found: C, 56.56; H, 3.38; Cl, 23.71; S, 10.55.

Reaction of the Adduct **28** *with Nitriles.* The reaction of 1.50 g (5.0 mmol) of **28** and 10.3 g (100 mmol) of benzonitrile in the presence of 1.0 g (7.5 mmol) of $AlCl_3$ was carried out similarly to the reaction with the ketenimine–SCl_2 adduct **17d** to give 0.22 g (13%) of 2,5,5-triphenyl-1,3-thiazolin-4-one (**29a**): mp 160–161°C (colorless plates from benzene–hexane); ir (Nujol) 1720 cm (C=O); ^1H nmr (δ) 7.2–7.7 (m, 13 H), 8.1–8.3 (m, 2 H); mass spectrum *m/e* 329 (M^+). Anal. Calcd for $C_{21}H_{15}NOS$: C, 76.57; H, 4.59; N, 4.25; S, 9.73. Found: C, 76.78; H, 4.33; N, 4.25; S, 9.73.

Similarly 5,5-diphenyl-2-*p*-tolyl-1,3-thiazolin-4-one (**29b**) was obtained in 13% yield from 28 and *p*-tolunitrile: mp 183–183.5°C (colorless plates from benzene); ir (Nujol) 1710 cm^{-1} (C=O); ^1H nmr (δ) 2.43 (s, 3 H, Me), 7.0–7.6 (m, 12 H), 7.9–8.2 (d, 2 H); ^{13}C nmr (ppm) 22.0, 75.0, 128.1, 128.5, 128.7, 129.0, 129.3, 129.8, 139.8, 191.8, 193.5; mass spectrum *m/e* 343 (M^+). Anal. Calcd for $C_{22}H_{17}NOS$: C, 76.94; H, 4.99; N, 4.08; S, 9.43. Found: C, 76.92; H, 4.91; N, 4.09; S, 9.03.

Reaction of the Adduct **28** *with N-Methylaniline.* A mixture of **28** (3.0 g, 10.1 mmol) and *N*-methylaniline (2.20 g, 20.5 mmol) in Et_2O (30 ml) was allowed to react for 5 h at room temperature. The resulting salt was filtered and the filtrate was concentrated to give oily material which was identified to be *N*-methyl-*N*-phenyl-1-chlorosulfenyldiphenylacetamide by ir, ^1H nmr, and mass spectra. A part of the oil (2.59 g, 7.0 mmol) was heated in refluxing benzene (30 ml) for 18 h, concentrated, and chromatographed to afford 1.14 g (49%) of 2,2-diphenyl-4-methylbenzothiazin-3-one (**30**) with 0.61 g (29%) of 3,3-diphenyloxindole. The benzothiazine was recrystallized from benzene–hexane to give colorless plates: mp 169–170°C; ir (Nujol) 1660 cm^{-1} (C=O); ^1H nmr (δ) 3.52 (s, 3 H, Me), 6.7–7.4 (m, 14 H); ^{13}C nmr (ppm) 33.1 (q), 59.9 (s), 116.7 (d), 122.9 (d), 123.2 (d), 127.1 (d), 127.7 (d), 127.9 (d), 128.8 (d), 138.5 (s), 140.0 (s), 168.4 (s); mass spectrum *m/e* 331 (M^+). Anal. Calcd for $C_{21}H_{17}ONS$: C, 76.10; H, 5.17; N, 4.23; S, 9.67. Found: C, 75.65; H, 4.90; N, 4.24; S, 9.67.

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10. The compound is considered to be obtained by hydrolysis of 2-*N*-tert-butylimidoyl-3-chlorobenzothiophene (or its 1 : 1 salt with SCl_2) which was formed by addition of SCl_2 to the C=C double bond followed by intramolecular cyclization.