agreement with those reported. The sulfides **1c,d,f** were known products[16,17,12] and their physical properties were in agreement with literature values.

***tert*-Butyl 1-(*p*-tolylthio)acetate (1a)** obtained in 80% yield had bp 115 °C (0.5 mm): n^{22}_D 1.5240; ^{1}H NMR δ 1.4 (s, 9 H), 2.3 (s, 3 H), 4.4 (s, 2 H), 7.1 (dd, 4 H). Anal. Calcd for $C_{13}H_{18}O_2S$: C, 65.5; H, 7.6. Found: C, 65.3; H, 7.7.

Phenyl 1-(*p*-tolylthio)acetate (1b) obtained in 56% yield after chromatography on silica gel petrol/diethyl ether 8:2 as eluant had mp 34–35 °C: ^{1}H NMR δ 2.3 (s, 3 H), 3.6 (s, 2 H), 7.1 (m, 9 H). Anal. Calcd for $C_{15}H_{14}O_2S$: C, 69.7; H, 5.5. Found: C, 69.4; H, 5.4.

1-(*p*-Tolylthio)-3,3-dimethyl-2-butanone (1e) obtained in 60% yield had bp 110 °C (0.05 mm): n^{25}_D 1.5408; ^{1}H NMR δ 1.1 (s, 9 H), 2.3 (s, 3 H), 3.8 (s, 2 H), 7.1 (dd, 4 H). Anal. Calcd for $C_{13}H_{18}OS$: C, 70.2; H, 8.2. Found: C, 70.3; H, 8.1.

1-(*p*-Tolylthio)-*N*,*N*-dimethylacetamide (1g) obtained in 53% yield after chromatography on silica gel with diethyl ether as eluant had mp 45 °C: ^{1}H NMR δ 2.3 (s, 3 H), 3.0 (d, 6 H), 3.7 (s, 2 H), 7.2 (dd, 4 H). Anal. Calcd for $C_{11}H_{15}NOS$: C, 63.1; H, 7.2; N, 6.7. Found: C, 63.0; H, 7.2; N, 6.6.

Preparation of *N*,*N*-Diethyl-4-methylbenzenesulfenamide (1h). This compound, prepared according to the general method[18] by reaction of *p*-tolylsulfenyl chloride and diethylamine in dry ether, had bp 84 °C (0.5 mm): n^{24}_D 1.5387; ^{1}H NMR δ 1.3 (t, 6 H), 2.4 (s, 3 H), 3.1 (q, 4 H), 7.2 (dd, 4 H). Anal. Calcd for $C_{11}H_{17}NS$: C, 67.6; H, 8.7; N, 7.2. Found: C, 67.3; H, 8.4; N, 7.0.

Oxidations: Typical Procedure. The sulfide (1 mmol) and 3.3 g of BSA (5×10^{-2} mmol) were magnetically stirred in 12.5 mL of buffer solution for 2 h at 20 °C, then $NaIO_4$ (2 mmol) was added, and the mixture was kept stirring for 2 h. Extraction with 3 portions (70 mL each) of diethyl ether and evaporation of the organic layer after drying gave the crude product that was purified by chromatography on silica gel with mixtures of ether and petrol as eluant. The yields and optical rotation values are reported in Table I.

Characteristics of the Sulfoxides 2a–f and of the Sulfinamide 2h. *tert*-Butyl α-(*p*-tolylsulfinyl)acetate (**2a**) had n^{22}_D 1.5262: ^{1}H NMR δ 1.4 (s, 9 H), 2.4 (s, 3 H), 3.7 (dd, 2 H), 7.4 (dd, 4 H). Phenyl 1-(*p*-tolylsulfinyl)acetate (**2b**) had n^{22}_D 1.5100: ^{1}H NMR δ 2.4 (s, 3 H), 3.7 (dd, 2 H), 7.2 (m, 9 H). Ethyl 1-(*p*-tolylsulfinyl)acetate (**2c**) had n^{22}_D 1.5453: ^{1}H NMR δ 1.3 (t, 3 H), 2.4 (s, 3 H), 3.7 (dd, 2 H), 4.1 (q, 2 H), 7.4 (dd, 4 H). Anal. Calcd for $C_{11}H_{14}O_3S$: C, 58.4; H, 6.2. Found: C, 58.2; H, 6.1. α-(*p*-Tolylsulfinyl)acetophenone (**2d**) had mp 75–80 °C: ^{1}H NMR δ 2.4 (s, 3 H), 4.3 (dd, 2 H), 7.3 (m, 7 H), 7.8 (m, 2 H). 1-(*p*-Tolylsulfinyl)-3,3-dimethyl-2-butanone (**2e**) had mp 93–96 °C: ^{1}H NMR δ 1.1 (s, 9 H), 2.5 (s, 3 H), 4 (dd, 2 H), 7.4 (dd, 4 H). 1-(Benzylsulfinyl)propan-2-one (**2f**) had mp 100–103 °C: ^{1}H NMR δ 2.3 (s, 3 H), 3.5 (dd, 2 H), 4.1 (dd, 2 H), 7.3 (s, 5 H). 1-(*p*-Tolylsulfinyl)-*N*,*N*-dimethylacetamide (**2g**) had mp 65–68 °C: ^{1}H NMR δ 2.4 (s, 3 H), 2.9 (two s, 6 H), 3.8 (dd, 2 H), 7.4 (dd, 4 H). *N*,*N*-Diethyl-4 methylbenzenesulfinamide (**2h**) had n^{20}_D 1.5320: ^{1}H NMR δ 1.1 (t, 6 H), 2.5 (s, 3 H), 3.2 (q, 4 H), 7.3 (dd, 4 H).

Preparation of β-Keto Sulfoxides. The (+)-(*R*)-α-(*p*-tolylsulfinyl)acetophenone (**2d**) prepared according to literature,[6] had mp 80–81 °C, $[\alpha]_D$ +179 (*c* 1, $CHCl_3$). The racemic α-(*p*-tolylsulfinyl)acetophenone (**2d**), mp 80–82 °C, was prepared by reaction of the sulfide (**1d**) with $NaIO_4$ in the usual conditions.

Reduction of β-Keto Sulfoxides. The same general procedures described above for the oxidation was followed with $NaBH_4$ (2 mmol) as reducing agent in pH 9 buffer solution. When the optically active β-keto sulfoxide, $[\alpha]_D$ +179, was used the β-hydroxy sulfoxide was obtained in 91% yield as crude product whereas the same compound was obtained in 80% yield starting from the racemic parent compound. Both these products were oxidized by the stoichiometric quantity of *m*-chloroperbenzoic acid at 20 °C for 18 h to the β-hydroxy sulfone in 65% and 74% yield, respectively, after purification by column chromatography (silica–light petroleum ether 1:1). The former had $[\alpha]_D$ +8.58 (*c* 1.2 in $CHCl_3$), mp 65–70 °C, while the latter had $[\alpha]_D$ +2.75 (*c* 3.92 in $CHCl_3$): mp 55–60 °C; ^{1}H NMR δ 2.4 (s, 3 H), 3.2 (m, 2 H), 3.6 (broad s, 1 H), 5.1 (dd, 1 H), 7.1 (m, 7 H), 7.6 (d, 2 H). When the borohydride reduction at pH 9 was repeated with β-keto sulfoxide **2d**, $[\alpha]_D$ +179, the oxidation of the intermediate diastereomeric mixture afforded the corresponding sulfone, $[\alpha]_D$ +1.14 (*c* 1 in $CHCl_3$), mp 45–50 °C.

Registry No. **1a**, 36304-27-5; **1b**, 94404-17-8; **1c**, 14738-27-3; **1d**, 33046-45-6; **1e**, 94404-18-9; **1f**, 10230-69-0; **1g**, 94404-19-0; **1h**, 24398-14-9; (*R*)-(+)-**2a**, 58059-08-8; (*S*)-(−)-**2a**, 94404-20-3; (*R*)-(+)-**2b**, 75340-59-9; (*R*)-(+)-**2c**, 72298-24-9; (*R*)-(+)-**2d**, 52154-24-2; (±)-**2d**, 86783-32-6; (*S*)-(−)-**2e**, 68326-60-3; (*R*)-(−)-**2f**, 69164-59-6; (*S*)-(−)-**2g**, 94404-21-4; (*R*)-(−)-**2h**, 94481-26-2; **3d**, 39201-98-4; **3e**, 39201-99-5; (+)-**4d**, 71899-81-5.

(16) Truce, W. F.; Steltenkamp, R. J. *J. Org. Chem.* **1962**, *27*, 2816.
(17) Knott, E. B. *J. Chem. Soc.* **1952**, 4099.
(18) Franklin, D. A. *Int. J. Sulf. Chem.* **1973**, *8*, 71.

C-(Methoxycarbonyl)ketene *N*-Imidoylimines. Synthesis and Rearrangement into Methyl 4,6-Diazahepta-2,4,6-trienoates. Cycloaddition Reactions with Isocyanides: Preparation of Imidazolines

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The ketene *N*-imidoylimines **12** are shown to be transitory intermediates formed by the reaction of isocyanides with sulfides **1** or by the reaction of imino chloro sulfides with sodium salts of α-cyano esters **3**. When the nitrogen atom of the imidoyl group bears a primary or secondary substituent, the ketene imines **12** are converted into diazatrienes **13** by a very fast 1,5-migration of the hydrogen atom of the imidoyl group. Diazatrienes **13** that bear a cyano group on C-1 of the R^1 group undergo an intramolecular [4 + 2] cycloaddition to form dihydropyrrolotriazines **14**. The diazatrienes **13** can be trapped by a regiospecific [1 + 4] cycloaddition with isocyanides to give imidazolines.

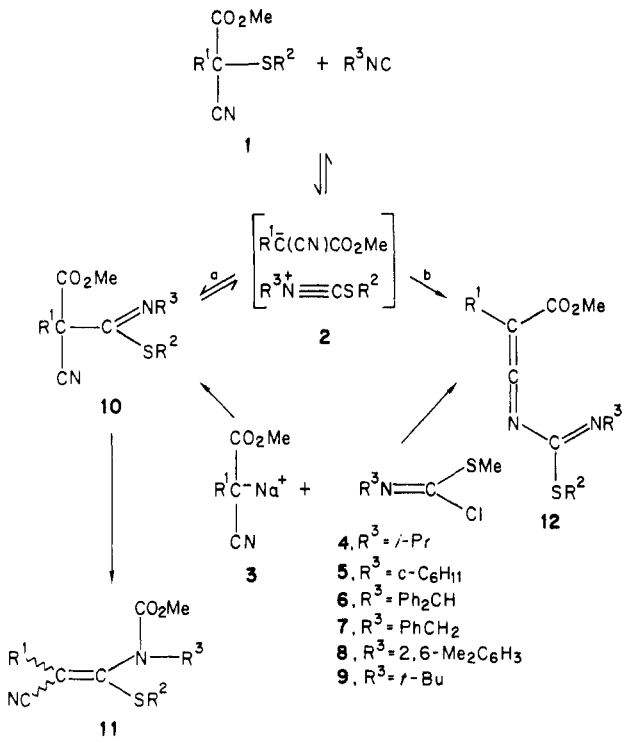
Introduction

In previous work, *tert*-butyl isocyanide and *tert*-octyl isocyanide were reported to insert into the carbon–sulfur bond of the electrophilic sulfides **1**.[1] The first step of the reaction occurs via the heterolytic and reversible cleavage of the C–S bond, giving an ion pair **2**. The rearrangement of **2** gives the thioimidates **10**, which are rapidly isomerized into stable *N*-vinylcarbamates **11**. Thioimidates and the isomeric carbamates can be also prepared by the reaction of (*tert*-butylimino)chloro(methylthio)methane (**9**) with the α-cyano ester salts **3** (Scheme I).[1] Only the carbon

(1) Morel, G.; Marchand, E.; Nguyen Thi, K. H.; Foucaud, A. *Tetrahedron Lett.* **1982**, *23*, 2023; *Tetrahedron* **1984**, *40*, 1075.

0022-3263/85/1950-0771$01.50/0

Scheme I



center of the ambident α-cyano ester anion is involved in these examples. We were attracted to the possibility that the nitrogen atom of this α-cyano ester anion could also be involved in these reactions to give ketene *N*-imidoylimines **12**. Such a rearrangement has been described with the same anions and bromophosphonium cations.[2] Ketene imines are also formed in the oxidative dimerization of some α-cyano esters by radical C–N coupling.[3,4] Consequently, we have explored the reaction of several salts **3** with the imino chloro sulfides **4–9**, and the rearrangement of a series of ion pairs **2** substituted by R^1 and R^3 groups having various steric and electronic effects, in the hope of obtaining the ketene *N*-imidoylimine **12**.[5]

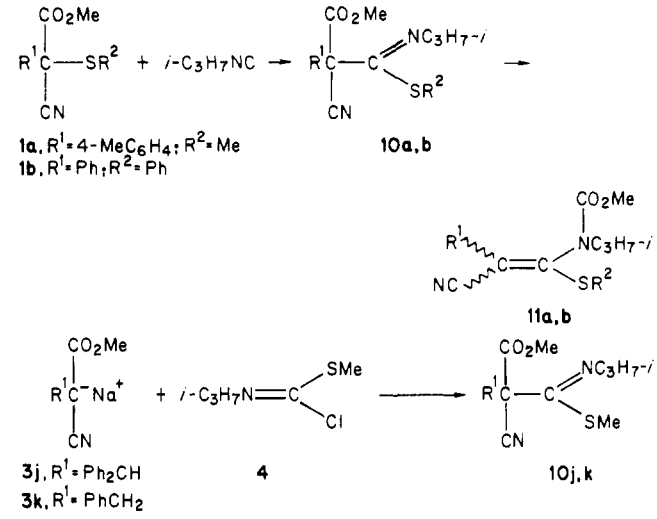
The [4 + 2] cycloadditions of *C*-vinylketene imines and ketene *N*-arylimines have attracted considerable attention for the synthesis of six-membered heterocycles.[6,7] The [1 + 4] cycloadditions of some ketene *N*-arylimines have been reported.[8] The [1 + 4] cycloadditions of isocyanides with the electron-deficient ketene *N*-imidoylimines **12** having ester and imino groups in conjugation with the cumulative system would be attractive for the synthesis of highly functionalized five-membered ring systems. We report here on the reactivities of the compounds **12** and the formation of some [1 + 4] cycloadducts with isocyanides.

Table I. Reaction of Sulfides 1 with Isocyanides

sulfide	isocyanide (R^3)	refluxing solvent	reactn time, h	products (% yield)[c]
1a	isopropyl	MeCN	50[a]	**11a** (63)
1b	isopropyl	MeCN	20[a]	**11b** (82)
1c	isopropyl	CH_2Cl_2	19[a]	**10c** (3), **14c** (69)
1d	isopropyl	CH_2Cl_2	65[a]	**10d** (11), **14d** (65)
1e	isopropyl	CH_2Cl_2	24[a]	**14e** (70)
1e	diphenylmethyl	CH_2Cl_2	40[b]	**10g** (6), **14g** (60)

[a] Time required for the entire conversion of the starting sulfide **1** in the presence of 2 equiv of isocyanide. [b] 1.2 equiv of isocyanide. [c] Isolated yield.

Scheme II



Results and Discussion

Only the carbamates **11a**, **11b** were obtained by refluxing isopropyl isocyanide and sulfides **1a**, **1b** in acetonitrile (Table I). There was no reaction in refluxing CH_2Cl_2. This result is explained by the fast and irreversible 1,3-migration of the CO_2Me group in the intermediates **10a**, **10b**.[1] The salts **3j** and **3k**, treated with the imino chloro sulfide **4**, gave the thioimidates **10j** and **10k** (Scheme II, Table III).

The formation of ketene imines **12** was not observed in these reactions, and we decided to increase the steric effect of the R^1 group. Sulfides **1c–e**, upon treatment with isopropyl isocyanide or diphenylmethyl isocyanide in refluxing CH_2Cl_2, were converted primarily into dihydro-1,3,5-triazines **14c–e,g** accompanied by lesser amounts of the corresponding thioimidates **10** (Table I). Structural assignments were based on spectral data (IR, ^1H and ^{13}C NMR, Table II) and were in good agreement with elemental analyses (Scheme III).

We postulate that the rearrangement of the ion pairs **2** can occur in two ways (Scheme I): process a leads to the thioimidates **10** and process b leads to the ketene imines **12**. These intermediates **12** give the diazatrienes **13** by 1,5-migration of the hydrogen atom in the α position to the nitrogen (Scheme III). The isomerization is similar to the fast 1,5-H shift recently reported in some imino ketenes[9] and diazadienes.[10] Finally, the triazines **14** are

(2) Leblanc, R.; Corre, E.; Soenen-Svilarich, M.; Chasle, M-F.; Foucaud, A. *Tetrahedron* **1972**, *28*, 4431. Corre, E.; Chasle, M-F.; Foucaud, A. *Tetrahedron* **1972**, *28*, 5055.

(3) De Jongh, H. A. P.; De Jonge, C. R. H. I.; Sinnige, H. J. M.; De Klein, W. J.; Huysmans, W. G. B.; Mijs, W. J.; Van den Hoek, W. J.; Smidt, J. *J. Org. Chem.* **1972**, *37*, 1960.

(4) Seveno, A.; Morel, G.; Foucaud, A.; Marchand, E. *Tetrahedron Lett.* **1977**, *38*, 3349. Morel, G.; Le Moing-Orliac, M. A.; Khamsitthideth, S.; Foucaud, A. *Tetrahedron* **1982**, *38*, 527.

(5) The ambident anion of **3** has a soft nucleophilic center, the carbon atom, and a hard center, the nitrogen atom. The reaction should be directed to the formation of the ketene imine if the steric hindrance of the carbon arising from R^1 is high and if the positive charge on the electrophilic center, due to the nature of the R^3 group, is high. See: Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533; *Science (Washington, D.C.)* **1966**, *151*, 172. Ho. T. L. "Hard and Soft Acids and Bases in Organic Chemistry"; Academic Press: New York, 1977.

(6) Ghosez, L.; O'Donnell, M. J. "Pericyclic Reactions"; Marchand, P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. II, Chapter 2.

(7) Sonveaux, E.; Ghosez, L. *J. Am. Chem. Soc.* **1973**, *95*, 5417. Gillard, M.; T'Kint, C.; Sonveaux, E.; Ghosez, L. *Ibid.* **1979**, *101*, 5837. Dondoni, A., Battaglia, A.; Giorgianni, P. *J. Org. Chem.* **1980**, *45*, 3766; *J. Org. Chem.* **1982**, *47*, 3998. Dondoni, A.; Battaglia, A.; Giorgianni, P.; Gilli, G.; Sacerdoti, M. *J. Chem. Soc., Chem. Commun.* **1977**, 43.

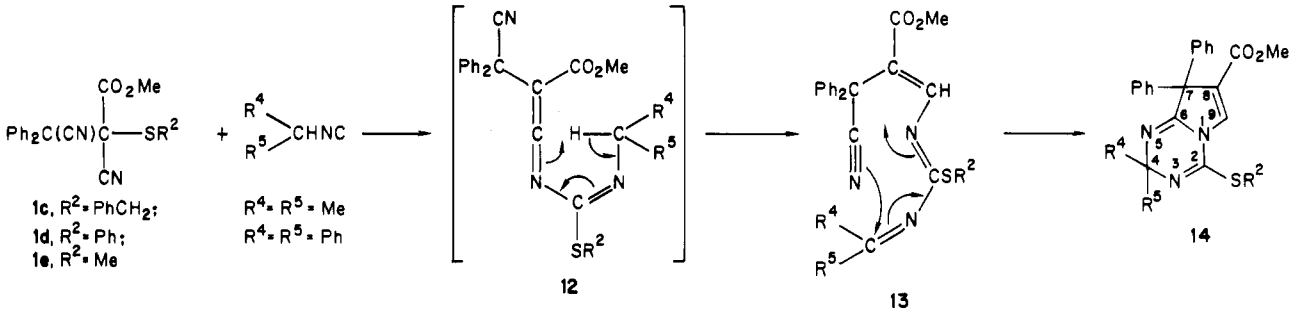
(8) Delstova, D. P.; Avetysian, E. A.; Gombaryan, N. P.; Knunyants, I. L. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1973**, 355. Obata, N.; Mizuno, H.; Koitabashi, T.; Tarizawa, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2287.

Table II. Selected ^{13}C NMR Shifts at 20.115 MHz for Some Triazines 14[a]

no.	C-6	C-7	C-8	C-9	C-2	C-4	C=O	OCH_3	$C(CH_3)_2$
14c	157.6	62.6	117.0	135.5	144.1	75.5	163.4	51.2	31.5
14d	158.0	62.7	117.1	136.1	143.8	76.4	163.4	51.2	31.0
14e	157.6	62.6	117.0	135.6	145.0	75.9	163.5	51.2	31.4

[a] Values are given in ppm and were obtained in $CDCl_3$ solutions referenced to Me_4Si.

Scheme III



	R^1	R^2	R^3	R^4	R^5
a	4-MeC_6H_4	Me	Me_2CH		
b	Ph	Ph	Me_2CH		
c	$Ph_2C(CN)$	$PhCH_2$		Me	Me
d	$Ph_2C(CN)$	Ph		Me	Me
e	$Ph_2C(CN)$	Me		Me	Me
f	$Ph_2C(CN)$	Me		$-(CH_2)_5-$	
g	$Ph_2C(CN)$	Me		Ph	Ph
h	$Ph_2C(CN)$	Me		Ph	H
i	$Ph_2C(CN)$	Me	2,6-$Me_2C_6H_3$		
j	Ph_2CH	Me	Me_2CH		
k	$PhCH_2$	Me	Me_2CH		
l	2,4,6-$Me_3C_6H_2$	Me		Me	Me
m	2,4,6-$Me_3C_6H_2$	Me		Ph	Ph
n	2,4,6-$Me_3C_6H_2$	Me		Ph	H
o	2,4,6-$Me_3C_6H_2$	Me	*t*-Bu		
p	$Ph_2C(Me)$	Me	2,6-$Me_2C_6H_3$		

formed from 13 by the intramolecular [4 + 2] cycloaddition of the cyano group with the neighboring diazadiene moiety (Scheme III). Some [4 + 2] cycloaddition reactions involving a cyano group have previously been described.[10-13]

Evidence for the Formation of Diazatrienes 13. When the reaction of sulfides **1c–e** with an excess of isopropyl isocyanide was carried out without solvent at room temperature, ^1H NMR indicated that the principal products were the diazatrienes **13**, generally in admixture with small quantities of compounds **10** and **14**. These diazatrienes are easily transformed in solution into the triazines **14** and were not isolated.

On the other hand, the reaction of the salt **3c** with the imino chloro sulfides **4–6**, which bear a secondary substituent on nitrogen, is sufficiently fast at room temperature that **13e–g** could be isolated before their conversion into the triazines **14** (Table III). Diazatrienes **13e–g** slowly converted into **14e–g** in $CHCl_3$ solution at room temperature. A small quantity of iminopyrroline **15** arising from the partial hydrolysis of **13e–g** was also obtained in these cyclizations (Scheme IV). The reaction of **3c** with **7** gave directly the dihydrotriazine **14h**, which was hydrolyzed and oxidized to the triazinone **17** (35%) in ether at room temperature. In this case, the intramolecular [4 + 2] cycloaddition with the cyano group was very fast and the diazatriene **13h** was not observed.

Table III. Reaction of Imino Chloro Sulfides with Methyl Cyanoacetate Salts 3 in THF at 20 °C

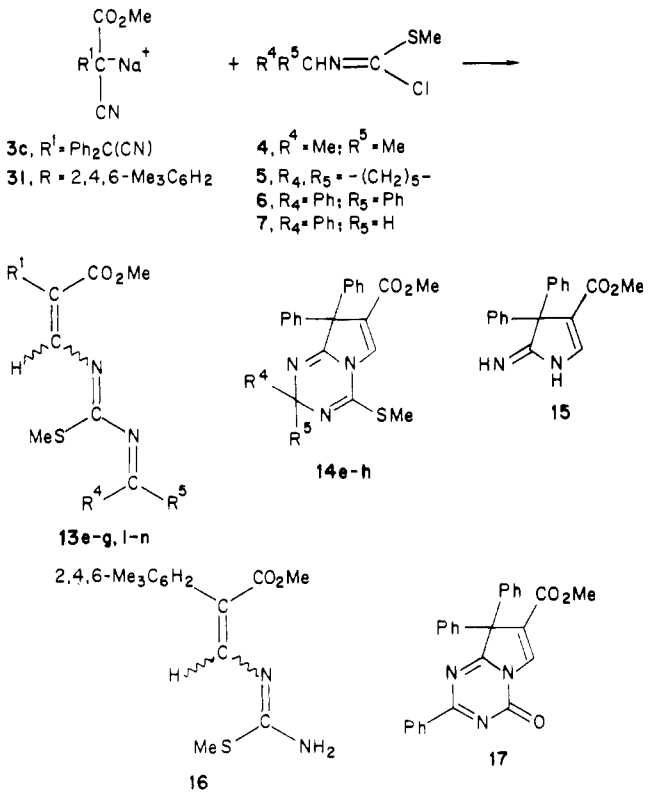
salt	imino chloro sulfide	reactn time, h	products (% yield)
3c	**4**	0.75	**13e** (46)
3c	**5**	1	**13f**[a]
3c	**6**	24	**13g**[b]
3c	**7**	0.5	*c*
3c	**8**	2	**10i** (14), **12i**[d]
3j	**4**	18	**10j** (60)[e]
3k	**4**	0.5	**10k** (66)
3l	**4**	0.5	**13l** (78)
3l	**6**	27	**13m** (67)
3l	**7**	1.5	**13n** (61)
3l	**9**	0.5	**12o**[f]
3p	**8**	2	**12p**[d]

[a] Observed then converted into **14f** (52%) by refluxing the reaction mixture for 1 h. [b] Observed then converted into **14g** (59%) after two days at 20 °C. [c] **13h** was not observed and gave **14h** by a fast reaction. [d] Observed then converted into imidazoline with an excess of 2,6-dimethylphenyl isocyanide. [e] The distillation of **10j** gave **11j** (40%). [f] Observed then converted into **26** with an excess of *tert*-butyl isocyanide.

The salt of methyl mesitylcyanoacetate (**3l**), which does not have the cyano group necessary for formation of **14**, reacted with **4**, **6**, or **7** to give diazatrienes **13l–n** (Scheme IV, Table III). The diazatrienes **13l** and **13n** were easily hydrolyzed to the isothiourea **16**. Ketene imines **12**, which undergo spontaneously the 1,5-H shift, were never observed. The methyl 4,6-diazahepta-2,4,6-trienoates **13e–**

(9) Maujean, A.; Marcy, G.; Chuche, J. *J. Chem. Soc., Chem. Commun.* **1980**, 92; *Tetrahedron Lett.* **1980**, *21*, 519.
(10) (a) Burger, K.; Penninger, S. *Synthesis* **1978**, 524. (b) Imming, P.; Mohr, R.; Müller, E.; Overheu, W.; Seitz, G. *Angew Chem., Int. Ed. Engl.* **1982**, *21*, 284.
(11) Oppolzer, W. *Angew Chem., Int. Ed. Engl.* **1972**, *11*, 1031.
(12) Matsuda, I.; Yamamoto, S.; Ishii, Y. *J. Chem. Soc. Perkin Trans. I* **1976**, 1523.
(13) Burger, K.; Penninger, S.; Grusel, M.; Daltrozzo, E. *J. Fluorine Chem.* **1980**, *15*, 1.

Scheme IV



g,**l**–**n** were characterized by ^{1}H NMR spectra and by chemical evidence.

Trapping of diazatrienes **13c** and **13e** (obtained in situ by the reaction of a large excess of isocyanide with **1**, without solvent, at room temperature) by [1 + 4] cycloaddition to isopropyl isocyanide gave the imidazolines **18** (41%) and **19** (37%) together with lesser amounts of triazines **14c** (15%) and **14e** (30%). Similar reactions of diazatrienes **13l** and **13m** with isopropyl or *tert*-butyl isocyanide yielded imidazolines **20**–**22**. Reaction of **13n** with *tert*-butyl isocyanide gave the imidazole **23** (Scheme V, Table V). These cycloaddition reactions were completely regioselective: only one diene system was involved.

These results show that the reaction of α-cyano ester salts **3** with imino chloro sulfides **4**–**7** is a better route to diazatrienes **13** than that starting with sulfides **1**. On the other hand, reaction of α-cyano ester salts **3a**–**c**,**j** with imino chloro sulfide **9** gives only the thioimidate **10**,[1] indicating that the electron-donating effect of the *tert*-butyl group favors process a (Scheme I). The diazatrienes are good materials for the synthesis of substituted imidazolines. Few examples of [1 + 4] cycloaddition reactions of isocyanides with azadiene or diazadienes to give pyrrole,[14] pyrazoles,[10b] or imidazoline[12] have been reported. Only one geometric isomer of the diazatrienes **13** and the imidazolines **18**–**22** was obtained; their stereochemistry was not determined.

Ketene Imines 12. In order to establish the formation of ketene imines **12**, we used tertiary substituents R^3 to avoid the transformation of **12** into the diazatrienes **13**. The imino chloro sulfides **8** and **9** were treated respectively with the salts **3c**, **3p**, and **3l** (Table III). The IR spectra of the crude products showed a signal at 2005–2020 cm^{-1}, in agreement with the ketenimine structure. The presence of the ketene imine was firmly established by trapping **12i** and **12p** with an excess of 2,6-dimethylphenyl isocyanide to give the imidazolines **24** and **25** and the [1 + 4] cycloadduct **26** was obtained by trapping **12o** with an excess of

Scheme V

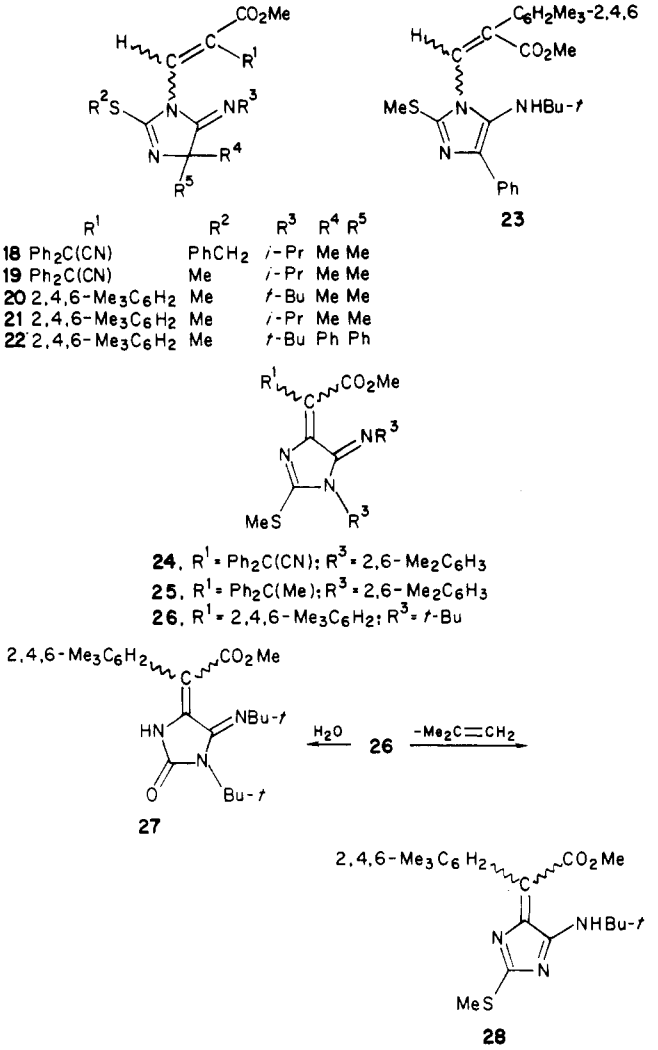


Table IV. Reactions of Sulfide 29 with Isocyanides

isocyanide (R^3)	reactn condn[c]	products (% yield)[d]
tert-butyl[a]	CH_2Cl_2, 15	**30** (72)
tert-butyl[a]	MeCN, 2	**33** (34), **34** (20)
isopropyl[a]	CH_2Cl_2, 24	**31** (10), **35** (70)
diphenylmethyl[b]	CH_2Cl_2, 75	**36** (80)

[a] 3 equiv. [b] 2 equiv. [c] Solvent, reflux time in hours. [d] Isolated yields.

tert-butyl isocyanide. On standing in air at room temperature, imidazoline **26** gave **27** by hydrolysis and **28** by a retroene reaction (Scheme V).[15] Ketene imine **12p** is less electrophilic than **12i** and **12o**; the latter two were trapped at room temperature, while trapping of **12p** required the reflux temperature of THF. These cycloadditions were regiospecific. The ester group, which was conjugated with the cumulative system and could participate in the cycloaddition,[2,16] was therefore not involved.

Reaction of Isocyanides with *N*-Methyl-3,3-diphenyl-4-cyano-4-(methylthio)succinimide (29). The sulfide **29** was also used to prepare intermediate ketene imines and diazatrienes. The thioimidate **30** was obtained by refluxing *tert*-butyl isocyanide and **29** in CH_2Cl_2, whereas ketene imine **32** was formed when the reaction was conducted in refluxing CH_3CN. The ketene imine **32** was

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Scheme VI

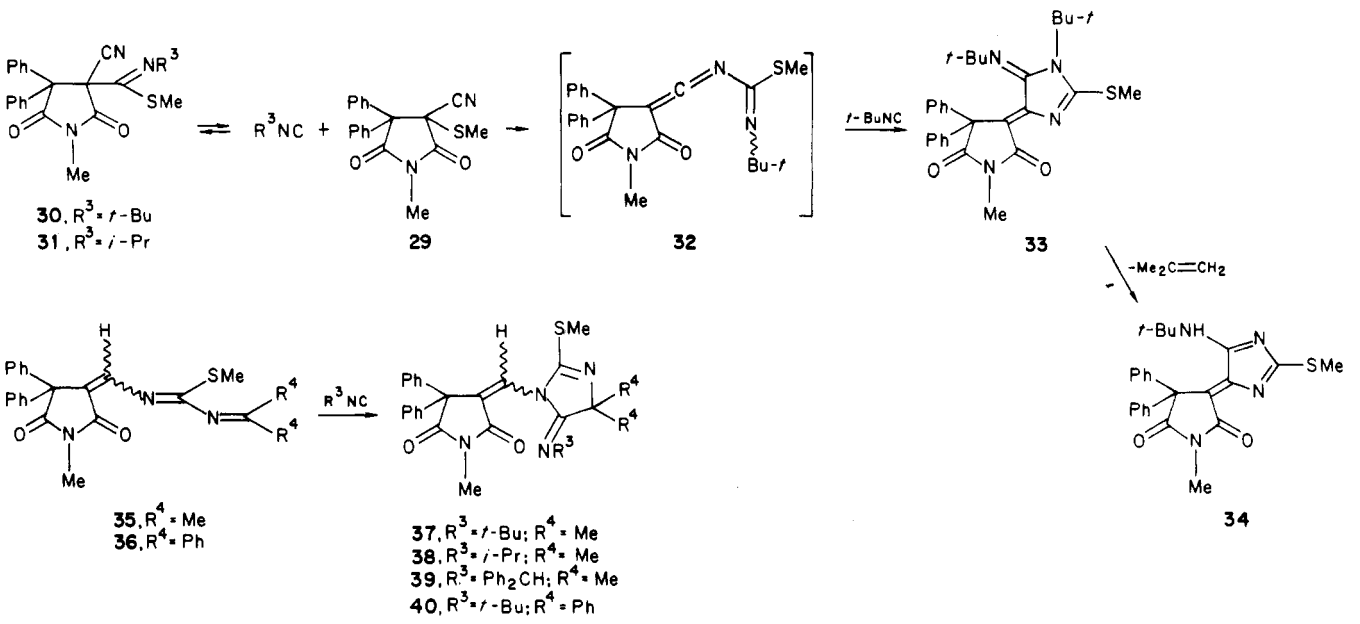

Table V. [1 + 4] Cycloadditions of Diazatrienes with Isocyanides

isocyanide (R^3)	diazatriene	reactn condn[a]	products (% yield)[b]
tert-butyl	**13l**	THF, 17	**20** (61)
isopropyl	**13l**	THF, 23	**21** (67)
tert-butyl	**13m**	THF, 110	**22** (60)
tert-butyl	**13n**	THF, 5	**23** (81)
tert-butyl	**35**	MeCN, 23	**37** (50)
isopropyl	**35**	MeCN, 16	**38** (60)
diphenylmethyl	**35**	MeCN, 18	**39** (44)
tert-butyl	**36**	MeCN, 92	**40** (50)

[a] Solvent, reflux time in hours. [b] Isolated yields.

trapped by an excess of *tert*-butyl isocyanide. The [1 + 4] cycloadduct **33** was converted into **34** by retroene reaction (Scheme VI). When the sulfide **29** was treated with isopropyl isocyanide or diphenylmethyl isocyanide, the thioimidate **31** and diazatrienes **35** or **36** were isolated (Table IV). The [1 + 4] cycloaddition of isocyanides to **35** and **36** gave the imidazolines **37–40** (Table V).

The formation of the thioimidate **30** was reversible according to the following observations. Refluxing **30** in CH_2Cl_2 partially decomposed it into the isocyanide and sulfide **29**. In refluxing acetonitrile with an excess of *tert*-butyl isocyanide, **30** gave compounds **33** and **34**. In the same way, the thioimidate **10c** was quantitatively transformed into the triazine **14c** when it was heated in CH_3CN for 21 h.

Therefore, the formation of the ketene *N*-imidoylimines **12** is favored when the carbon atom of the carbanion is hindered by a large R^1 group and when the R^3 group has a low electron-donating effect. The rearrangement of ketene imines **12** into **13** provides a new route to the synthesis of 1,3-diaza-1,3-diene equivalents, which are not easily available by other methods. These diazadienes, which undergo Diels–Alder reactions,[17] can also participate in [1 + 4] cycloadditions with isocyanides.

Experimental Section

Melting points are uncorrected. Mass spectra were obtained on a Varian MAT 311 spectrometer. IR spectra were recorded as suspensions in Nujol, unless otherwise indicated, with a Perkin Elmer 225 spectrometer. NMR spectra (internal standard Me_4Si) were taken in $CDCl_3$ unless stated otherwise, on Bruker WP 80 and FT WP 80 spectrometers. Elemental analyses were performed by the analytical laboratory, Centre National de la Recherche Scientifique.

General Procedure for the Reaction of Isocyanides with Sulfides in a Solvent at Reflux. An excess of isocyanide was added to the sulfides[1] **1a–e** and **29** (5 mmol) in CH_2Cl_2 or CH_3CN (15 mL). The mixture was maintained at reflux under nitrogen for the time indicated in Tables I and IV. After concentration the residue was analyzed by NMR. The crude product was precipitated by addition of ether or distilled under reduced pressure then purified by recrystallization.

Methyl *N*-Isopropyl-*N*-[2-cyano-2-(*p*-methylphenyl)-1-(methylthio)vinyl]carbamate (11a). Isomer *E*: mp 102 °C (MeOH); IR 2197, 1710 cm^{-1}; ^1H NMR δ 1.47 (d, J = 6 Hz, 6 H), 2.16 (s, 3 H), 2.39 (s, 3 H), 3.82 (s, 3 H), 4.38 (m, J = 6 Hz, 1 H), 7.35 (m, 4 H); ^{13}C NMR δ 15.4, 20.7, 21.4, 52.5, 53.4, 114.3, 117.6, 129.1, 129.4, 139.7, 152.6, 154.4. Anal. Calcd for $C_{16}H_{20}N_2O_2S$: C, 63.15; H, 6.57; N, 9.21; S, 10.52. Found: C, 63.16; H, 6.56; N, 8.99; S, 10.34. **Isomer *Z***: mp 69 °C (EtOH); IR 2197, 1709 cm^{-1}; ^1H NMR δ 1.07 (d, J = 6 Hz, 6 H), 2.33 (s, 3 H), 2.40 (s, 3 H), 3.70 (s, 3 H), 3.98 (m, J = 6 Hz, 1 H), 7.18 (m, 4 H). Anal. Calcd for $C_{16}H_{20}N_2O_2S$: C, 63.15; H, 6.57; N, 9.21; S, 10.52. Found: C, 63.20; H, 6.80; N, 9.41; S, 10.51.

Methyl *N*-Isopropyl-*N*-[2-cyano-2-phenyl-1-(phenylthio)vinyl]carbamate (11b). The crude oil was distilled, bp 190 °C (0.02 torr). **Isomer *Z***: mp 105 °C (MeOH); ^1H NMR δ 0.95 (d, J = 6 Hz, 6 H), 3.48 (s, 3 H), 3.86 (m, J = 6 Hz, 1 H), 7.4 (m, 5 H). Anal. Calcd for $C_{20}H_{20}N_2O_2S$: C, 68.18; H, 5.68; N, 7.95; S, 9.09. Found: C, 68.40; H, 5.78; N, 8.10; S, 8.83. **Isomer *E*** (in a mixture of the two isomers): ^1H NMR δ 1.20 (d, J = 6 Hz, 6 H), 3.76 (s, 3 H), 4.02 (m, 1 H), 7.4 (m, 5 H).

Methyl 3-(benzylthio)-2-cyano-2-(cyanodiphenylmethyl)-3-(isopropylimino)propanoate (10c): mp 158 °C (MeOH); IR 2224, 1750, 1613 cm^{-1}; ^1H NMR δ 0.91 (d, J = 6 Hz, 3 H), 1.15 (d, J = 6 Hz, 3 H), 3.66 (s, 3 H), 4.15 (m, 1 H), 4.17 (s, 2 H), 7.3 (m, 15 H).

Methyl 2-cyano-2-(cyanodiphenylmethyl)-3-(phenylthio)-3-(isopropylimino)propanoate (10d): mp 118 °C (ether/petroleum ether); IR 2230, 1749, 1631 cm^{-1}; ^1H NMR δ 0.85 (d, J = 6 Hz, 3 H), 1.07 (d, J = 6 Hz, 3 H), 3.42 (s, 3 H), 4.11 (m, J = 6 Hz, 1 H), 7.3 (m, 15 H). Anal. Calcd for $C_{28}H_{25}N_3O_2S$: C, 71.94; H, 5.35; N, 8.99; S, 6.85. Found: C, 71.88; H, 5.26; N, 9.06; S, 6.89.

Methyl 2-cyano-2-(cyanodiphenylmethyl)-3-[(diphenylmethyl)imino]-3-(methylthio)propanoate (10g): mp 173 °C (EtOH); IR 2239, 1738, 1635 cm^{-1}; ^1H NMR δ 2.28 (s, 3 H), 3.60 (s, 3 H), 6.15 (s, 1 H), 7.2 (m, 20 H).

2-(Benzylthio)-4,4-dimethyl-7,7-diphenyl-8-(methoxycarbonyl)-1,3,5-triazabicyclo[4.3.0]nona-2,5,8-triene (14c): mp 109 °C (EtOH); IR 1711, 1695 cm^{-1}; ^1H NMR δ 1.40 (s, 6 H), 3.57 (s, 3 H), 4.27 (s, 2 H), 7.30 (s, 15 H), 7.67 (s, 1 H). Anal. Calcd

(17) Boger, D. L. *Tetrahedron* **1983**, *39*, 2869.

for $C_{29}H_{27}N_3O_2S$: C, 72.34; H, 5.61; N, 8.73; S, 6.65. Found: C, 72.22; H, 5.65; N, 8.73; S, 6.65.

4,4-Dimethyl-7,7-diphenyl-8-(methoxycarbonyl)-2-(phenylthio)-1,3,5-triazabicyclo[4.3.0]nona-2,5,8-triene (14d): mp 142 °C (MeOH); IR 1708, 1691, 1584, 1574 cm^{-1}; ^1H NMR δ 1.32 (s, 6 H), 3.57 (s, 3 H), 7.3 (m, 15 H), 7.77 (s, 1 H). Anal. Calcd for $C_{28}H_{25}N_3O_2S$: C, 71.94; H, 5.35; N, 8.99; S, 6.85. Found: C, 72.18; H, 5.26; N, 9.07; S, 6.89.

4,4-Dimethyl-7,7-diphenyl-8-(methoxycarbonyl)-2-(methylthio)-1,3,5-triazabicyclo[4.3.0]nona-2,5,8-triene (14e): mp 181 °C (MeOH); IR 1737, 1706, 1688, 1602, 1580, 1572 cm^{-1}; ^1H NMR δ 1.35 (s, 6 H), 2.40 (s, 3 H), 3.58 (s, 3 H), 7.28 (s, 10 H), 7.70 (s, 1 H). Anal. Calcd for $C_{23}H_{23}N_3O_2S$: C, 68.14; H, 5.67; N, 10.37; S, 7.90. Found: C, 67.93; H, 5.70; N, 10.18; S, 7.72.

8-(Methoxycarbonyl)-2-(methylthio)-4,4,7,7-tetraphenyl-1,3,5-triazabicyclo[4.3.0]nona-2,5,8-triene (14g): mp 233 °C ($MeOH/CHCl_3$); IR 1708, 1583, 1566 cm^{-1}; ^1H NMR δ 2.50 (s, 3 H), 3.54 (s, 3 H), 7.2 (m, 20 H), 7.67 (s, 1 H). Anal. Calcd for $C_{33}H_{27}N_3O_2S$: C, 74.85; H, 5.10; N, 7.93; S, 6.04. Found: C, 74.60; H, 5.04; N, 7.71; S, 6.12.

2-Cyano-3,3-diphenyl-2-[(*tert*-butylimino)(methylthio)methyl]-*N*-methylsuccinimide (30): mp 132 °C (petroleum ether); IR 2240, 1777, 1707 cm^{-1}; ^1H NMR δ 1.00 (s, 9 H), 2.65 (s, 3 H), 3.10 (s, 3 H), 7.4 (m, 10 H). Anal. Calcd for $C_{24}H_{25}N_3O_2S$: C, 68.73; H, 5.96; N, 10.02; S, 7.63. Found: C, 68.89; H, 6.08; N, 9.83; S, 7.56.

2-Cyano-3,3-diphenyl-2-[(methylthio)(isopropylimino)methyl]-*N*-methylsuccinimide (31): mp 150 °C (chloroforme/petroleum ether); IR 2234, 1775, 1703, 1610 cm^{-1}; ^1H NMR δ 0.74 (d, J = 6 Hz, 3 H), 0.95 (d, J = 6 Hz, 3 H), 2.27 (s, 3 H), 3.09 (s, 3 H), 3.81 (m, 1 H), 7.4 (m, 10 H). Anal. Calcd for $C_{23}H_{23}N_3O_2S$: C, 68.14; H, 5.67; N, 10.37; S, 7.90. Found: C, 68.23; H, 5.83; N, 10.06; S, 8.01.

2-[2,4-Diaza-5-methyl-3-(methylthio)hexa-2,4-dien-1-ylidene]-3,3-diphenyl-*N*-methylsuccinimide (35): mp 233 °C (MeOH); IR 1754, 1748, 1689, 1654, 1628, 1539 cm^{-1}; ^1H NMR δ 1.76 (s, 6 H), 2.01 (s, 3 H), 3.13 (s, 3 H), 7.3 (s, 10 H), 7.80 (s, 1 H); ^{13}C NMR δ 178.3, 174.5, 172.7, 171.0, 139.8, 138.4, 129.2, 127.9, 127.3, 123.7, 61.3, 25.1, 24.8, 13.8; MS calcd for $C_{23}H_{23}N_3O_2S$, m/e 405.1511 (M^+), found m/e 405.1501. Anal. Calcd for $C_{23}H_{23}N_3O_2S$: C, 68.14; H, 5.67; N, 10.37; S, 7.90. Found: C, 67.88; H, 5.74; N, 10.24; S, 7.90.

2-[2,4-Diaza-5,5-diphenyl-3-(methylthio)penta-2,4-dien-1-ylidene]-3,3-diphenyl-*N*-methylsuccinimide (36): mp 183 °C (EtOH); IR 1749, 1691, 1636, 1590, 1568, 1508 cm^{-1}; ^1H NMR δ 1.85 (s, 3 H), 3.12 (s, 3 H), 7.26 (s, 10 H), 7.38 (s, 10 H), 8.03 (s, 1 H). Anal. Calcd for $C_{33}H_{27}N_3O_2S$: C, 74.85; H, 5.10; N, 7.93; S, 6.04. Found: C, 74.94; H, 5.20; N, 7.83; S, 6.07.

2-[1-*tert*-Butyl-5-(*tert*-butylimino)-2-(methylthio)-2-imidazol-4-ylidene]-3,3-diphenyl-*N*-methylsuccinimide (33): mp 200 °C (MeOH); IR 1771, 1702, 1509, 1503 cm^{-1}; ^1H NMR δ 1.02 (s, 9 H), 1.37 (s, 9 H), 2.40 (s, 3 H), 3.15 (s, 3 H), 7.20 (m, 10 H); ^{13}C NMR δ 183.5, 176.3, 172.4, 158.2, 150.2, 138.9, 137.4, 129.2, 128.7, 128.4, 127.3, 72.9, 64.9, 57.8, 57.1, 29.9, 28.3, 25.5, 15.4; MS calcd for $C_{29}H_{34}N_4O_2S$, m/e 502.2402 (M^+), found m/e 502.2400. Anal. Calcd for $C_{29}H_{34}N_4O_2S$: C, 69.32; H, 6.77; N, 11.15; S, 6.37. Found: C, 69.33; H, 6.82; N, 11.17; S, 6.35.

2-[4-(*tert*-Butylamino)-2-(methylthio)-5-isoimidazol-5-ylidene]-3,3-diphenyl-*N*-methylsuccinimide (34): mp 272 °C ($CHCl_3$/ether); IR 3335, 1742, 1682, 1568 cm^{-1}; ^1H NMR δ 1.13 (s, 9 H), 2.76 (s, 3 H), 3.17 (s, 3 H), 5.07 (br s, 1 H), 7.2 (m, 10 H); MS calcd for $C_{25}H_{26}N_4O_2S$, m/e 446.1776 (M^+), found m/e 446.1787.

Reaction of Isocyanides with Sulfides 1 at Room Temperature. Isopropyl isocyanide (1.7 g, 25 mmol) was added to sulfide **1c** (2.06 g, 5 mmol). After 19 h, ^1H NMR analysis of the reaction mixture showed the presence of **10c**, **13c**, and **18** in the ratio 10:75:15. **13c**: ^1H NMR δ 1.97 (s, 6 H), 3.46 (s, 3 H), 3.76 (s, 2 H), 7.27 (m, 15 H), 7.72 (s, 1 H). The reaction mixture was maintained for 5 days at room temperature to give **10c**, **14c**, and **18** in the ratio 20:30:50 (by ^1H NMR). Crystallization from ether gave **10c** (9%), **14c** (15%), and **18**: mp 164 °C (MeOH) (41%); IR 2236, 1730, 1683, 1626, 1586 cm^{-1}; ^1H NMR δ 1.04 (d, J = 6 Hz, 6 H), 1.25 (s, 6 H), 3.50 (s, 3 H), 3.85 (m, 1 H), 4.30 (s, 2 H), 7.3 (m, 16 H). Anal. Calcd for $C_{33}H_{34}N_4O_2S$: C, 72.00; H, 6.18; N, 10.18; S, 5.81. Found: C, 71.83; H, 6.19; N, 10.17; S, 6.02.

The sulfide **1e**, subjected to the same conditions gave **13e** after 19 h and after 15 days, a mixture of **14e** and **19** in the ratio 45:55. Crystallization from ether gave **14e** (30%) and **19** (37%): mp 172 °C (MeOH); ^1H NMR δ 1.03 (d, J = 7 Hz, 6 H), 1.24 (s, 6 H), 2.49 (s, 3 H), 3.57 (s, 3 H), 3.86 (m, 1 H), 7.3 (m, 11 H); MS calcd for $C_{27}H_{30}N_4O_2S$, m/e 474.2089 (M^+), found m/e 474.2120.

In the same way, after 17 h, sulfide **1d** gave partially **10d**, **13d**, and **14d** in the ratio 25:50:25 (by ^1H NMR). **13d**: ^1H NMR δ 1.75 (s, 6 H), 3.44 (s, 3 H), 7.3 (m, 15 H), 7.75 (s, 1 H). **13d**, not purified, was slowly transformed into **14d**.

Reaction of Imino Chloro Sulfides 4–7 with the Salts 3. Preparation of Diazatrienes 13, Thioimidates 10j and 10k, and Triazines 14f and 14h. To a solution of methylsulfenyl chloride (10 mmol) in CCl4 was added dropwise with stirring under dry N_2 a solution of isocyanide (12 mmol) in THF (15 mL). Immediately the red color of MeSCl disappeared. The reaction mixture was stirred for a further 10 min at ambient temperature. To this solution of imino chloro sulfide was added a solution of sodium salt **3** (10 mmol) in THF (30 mL). The mixture was stirred for the time indicated in Table III and filtered. Evaporation of the filtrate, extraction of the residue with ether and then addition of petroleum ether gave crystalline diazatrienes **13e** and **13l–13n**.

Methyl 2-(cyanodiphenylmethyl)-4,6-diaza-7-methyl-5-(methylthio)octa-2,4,6-trienoate (13e): mp 127 °C; IR 2224, 1704, 1652, 1529 cm^{-1}; ^1H NMR (C_6D_6) δ 1.45 (s, 6 H), 1.82 (s, 3 H), 3.10 (s, 3 H), 7.0–8.6 (m, 10 H), 7.97 (s, 1 H). Anal. Calcd for $C_{23}H_{23}N_3O_2S$: C, 68.14; H, 5.67; N, 10.37; S, 7.90. Found: C, 67.87; H, 5.59; N, 10.36; S, 7.54.

Methyl 4-aza-2-(cyanodiphenylmethyl)-5-(cyclohexylideneamino)-5-(methylthio)penta-2,4-dienoate (13f): oil; ^1H NMR δ 1.57 (br, 6 H), 1.87 (s, 3 H), 2.15 (br, 4 H), 3.40 (s, 3 H), 7.3 (m, 10 H), 7.75 (s, 1 H).

[7,7-Diphenyl-8-(methoxycarbonyl)-2-(methylthio)-3,5-triazabicyclo[4.3.0]nona-2,5,8-triene]-4-spirocyclohexane (14f): mp 138 °C (MeOH); IR 1703, 1676, 1581, 1569 cm^{-1}; ^1H NMR δ 1.59 ((br s, 10 H), 2.40 (s, 3 H), 3.59 (s, 3 H), 7.27 (s, 10 H), 7.70 (s, 1 H). Anal. Calcd for $C_{26}H_{27}N_3O_2S$: C, 70.11; H, 6.06; N, 9.43; S, 7.19. Found: C, 69.93; H, 6.09; N, 9.35; S, 6.92.

Methyl 2-(cyanodiphenylmethyl)-4,6-diaza-7,7-diphenyl-5-(methylthio)hepta-2,4,6-trienoate (13g): oil ^1H NMR δ 1.69 (s, 3 H), 3.34 (s, 3 H), 7.3 (m, 20 H), 7.94 (s, 1 H).

Methyl 4,6-diaza-7-methyl-5-(methylthio)-2-(2,4,6-trimethylphenyl)octa-2,4,6-trienoate (13l): mp 90 °C; IR 1700, 1694, 1657, 1540, 1511 cm^{-1}; ^1H NMR δ 2.02 (s, 6 H), 2.11 (s, 9 H), 2.29 (s, 3 H), 3.67 (s, 3 H), 6.82 (s, 2 H), 7.85 (s, 1 H); MS calcd for $C_{18}H_{24}N_2O_2S$, m/e 332.1558 (M^+), found m/e 332.1558.

Methyl 4,6-diaza-7,7-diphenyl-5-(methylthio)-2-(2,4,6-trimethylphenyl)hepta-2,4,6-trienoate (13m): mp 135 °C (ether/petroleum ether); IR 1696, 1615, 1588, 1572, 1522 cm^{-1}; ^1H NMR δ 2.00 (s, 9 H), 2.25 (s, 3 H), 3.64 (s, 3 H), 6.80 (s, 2 H), 7.4 (m, 10 H), 8.05 (s, 1 H). Anal. Calcd for $C_{28}H_{28}N_2O_2S$: C, 73.68; H, N, 6.14; S, 7.01. Found: C, 73.69; H, 6.30; N, 6.09; S, 7.03.

Methyl 4,6-diaza-5-(methylthio)-7-phenyl-2-(2,4,6-trimethylphenyl)hepta-2,4,6-trienoate (13n): mp 128 °C; IR 1699, 1623, 1574, 1528 cm^{-1}; ^1H NMR δ 2.14 (s, 6 H), 2.23 (s, 3 H), 2.30 (s, 3 H), 3.70 (s, 3 H), 6.84 (s, 2 H), 7.4–7.8 (m, 5 H), 8.27 (s, 1 H), 8.30 (s, 1 H); MS calcd for $C_{22}H_{24}N_2O_2S$, m/e 380.1558 (M^+), found m/e 380.1571.

Methyl 2-cyano-2-(diphenylmethyl)-3-(methylthio)-3-(isopropylimino)propanoate (10j): oil; ^1H NMR δ 0.86, 1.01 (2 d, J = 6 Hz, 6 H), 2.12 (s, 3 H), 3.55 (s, 3 H), 3.95 (m, 6 Hz, 1 H), 5.30 (s, 1 H), 7.4 (m, 10 H).

The distillation of **10j** gave the carbamate **11j**: bp 210 °C (0.02 torr); mp 99 °C (MeOH) (80%); ^1H NMR δ 1.25, 1.37 (2 d, J = 7 Hz, 6 H), 2.30 (s, 3 H), 3.35 (s, 3 H), 4.10 (m, J = 7 Hz, 1 H), 5.08 (s, 1 H), 7.25 (s, 10 H). Anal. Calcd for $C_{22}H_{24}N_2O_2S$: C, 69.47; H, 6.31; N, 7.36; S, 8.42. Found: C, 69.46; H, 6.12; N, 7.37; S, 8.52.

Methyl 2-benzyl-2-cyano-3-(methylthio)-3-(isopropylimino)propanoate (10k): oil; bp 170 °C (0.02 torr); ^1H NMR δ 1.18, 1.25 (2 d, J = 6 Hz, 6 H), 2.44 (s, 3 H), 3.54 (s, 2 H), 3.71 (s, 3 H), 4.12 (m, J = 6 Hz, 1 H), 7.30 (s, 5 H). Anal. Calcd for $C_{16}H_{20}N_2O_2S$: C, 63.15; H, 6.57; N, 9.21; S, 10.52. Found: C, 63.39; H, 6.40; N, 9.05; S, 10.52.

8-(Methoxycarbonyl)-2-(methylthio)-4,7,7-triphenyl-1,3,5-triazabicyclo[4.3.0]nona-2,5,8-triene (14h): oil; ^1H NMR

δ 2.47 (s, 3 H), 3.62 (s, 3 H), 6.36 (s, 1 H), 7.3 (m, 15 H), 7.71 (s, 1 H).

8-(Methoxycarbonyl)-4,7,7-triphenyl-1,3,5-triazabicyclo-[4.3.0]nona-3,5,8-trien-2-one (17): mp 256 °C ($CHCl_3$/MeOH); IR 1702, 1603, 1585, 1568 cm^{-1}; ^1H NMR δ 3.77 (s, 3 H), 7.35 (s, 10 H), 8.30 (s, 1 H), 7.3–8.5 (m, 5 H); MS calcd for $C_{26}H_{19}N_3O_3$, *m/e* 421.1426 (M^+), found *m/e* 421.1434. Anal. Calcd for $C_{26}H_{19}N_3O_3$: C, 74.10; H, 4.51; N, 9.97. Found: C, 74.19; H, 4.36; N, 9.90.

Hydrolysis of Diazatrienes 13. When the diazatrienes (crystallized or in solution) were exposed to air moisture, a slow hydrolysis gave **15** from **13c–g** or **16** from **13l** and **13n**. In this case, the benzaldehyde was observed by ^1H NMR.

4,4-Diphenyl-5-imino-3-(methoxycarbonyl)-2-pyrroline (15): mp 272 °C (MeOH); IR 3395, 1652, 1529 cm^{-1}; ^1H NMR δ 3.55 (s, 3 H), 4.50 (br, 2 H) 7.23 (s, 10 H), 7.62 (s, 1 H); MS calcd for $C_{18}H_{16}N_2O_2$, *m/e* 292.1212 (M^+), found 292.1206. Anal. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.97; H, 5.47; N, 9.58. Found: C, 73.74; H, 5.41;, N, 9.40.

Methyl 5-amino-4-aza-5-(methylthio)-2-(2,4,6-trimethylphenyl)penta-2,4-dienoate (16): mp 196 °C (MeOH); IR 3435, 3000, 1687, 1640, 1600, 1504 cm^{-1}; ^1H NMR δ 2.00 (s, 6 H), 2.15 (s, 3 H), 2.19 (s, 3 H), 3.60 (s, 3 H), 6.42 (br, 2 H), 6.88 (s, 2 H), 8.15 (s, 1 H). Anal. Calcd for $C_{15}H_{20}N_2O_2S$: C, 61.64; H, 6.84; N, 9.58; S, 10.95. Found: C, 61.59; H, 6.83; N, 9.53; S, 10.75.

Preparation and Trapping Reaction of Ketene Imines 12. Reaction of Imino Chloro Sulfide 8 with 3c. The procedure was identical with that described for the preparation of **13**. The iminochloro sulfide **8** (10 mmol) was treated with salt **3c** (10 mmol) to give a mixture of **10i** and **12i**. **12i**: IR 2022, 1717 cm^{-1}. To this crude reaction product was added 2,6-dimethylphenyl isocyanide (1.57 g, 12 mmol) in THF (15 mL). The mixture was stirred under N_2 at room temperature for 16 h. The solvent was removed at reduced pressure. The residue, extracted with ether, gave **10i** and **24** which were separated by fractional crystallization from MeOH. **24**: mp 191 °C (MeOH) (47%, yield based on **3c** consumed); IR 1730, 1660, 1490 cm^{-1}; ^1H NMR δ 1.88 (s, 6 H), 1.97 (s, 6 H), 2.17 (s, 3 H), 3.09 (s, 3 H), 6.55 (s, 3 H), 6.79 (m, 3 H), 7.4 (m, 10 H). Anal. Calcd for $C_{37}H_{34}N_4O_2S$: C, 74.24; H, 5.68; N, 9.36; S, 5.35. Found: C, 74.39; H, 5.68; N, 9.51; S, 5.40. **10i**: mp 161 °C (MeOH) (14%); IR 1746, 1627, 1585 cm^{-1}; ^1H NMR δ 1.91 (s, 6 H), 2.32 (s, 3 H), 3.75 (s, 3 H), 6.88 (s, 3 H), 7.3–7.9 (m, 10 H). Anal. Calcd for $C_{28}H_{25}N_3O_2S$: C, 71.94; H, 5.35; N, 8.99; S, 6.85. Found: C, 72.12; H, 5.38; N, 8.90; S, 6.96.

Reaction of Imino Chloro Sulfide 8 with 3p. In the same way, the imino chloro sulfide **8** (10 mmol) was treated with **3p** (10 mmol) to give **12p** (IR 2005, 1715 cm^{-1}). To the crude reaction product was added 2,6-dimethylphenyl isocyanide (1.57 g, 12 mmol) in THF (15 mL). The mixture was heated at reflux for 16 h under nitrogen. The reaction mixture was filtered and concentrated. **25** was precipitated by addition of methanol: mp 160 °C (MeOH) (61%); IR 1726, 1659, 1501 cm^{-1}; ^1H NMR δ 1.95 (s, 6 H), 1.97 (s, 3 H), 2.02 (s, 6 H), 2.33 (s, 3 H), 3.35 (s, 3 H), 6.53 (s, 3 H), 6.75 (m, 3 H), 8.35 (m, 10 H); MS calcd for $C_{37}H_{37}N_3O_2S$, *m/e* 587.2606 (M^+), found *m/e* 587.2609.

Reaction of Imino Chloro Sulfide 9 with 3l. In the same way, the imino chloro sulfide **9** (10 mmol) was treated with **3l** (10 mmol) to give **12o** (IR 2015, 1711 cm^{-1}). To this crude reaction product was added *tert*-butyl isocyanide (1.0 g, 12 mmol) in THF (15 mL). The mixture was stirred under N_2 at room temperature for 5 h. The reaction mixture was concentrated and purified by column chromatography (silica gel) with ether as eluant to give **26** as an oil: ^1H NMR δ 1.02 (s, 9 H), 1.35 (s, 9 H), 2.25 (s, 9 H), 2.52 (s, 3 H), 3.65 (s, 3 H), 6.75 (s, 2 H). On standing at room temperature, in the presence of air moisture, **26** gave slowly **27** and **28**.

1-*tert*-Butyl-5-(*tert*-butylimino)-4-[(2,4,6-trimethylphenyl)(methoxycarbonyl)methylene]imidazolidin-2-one (27): mp 163 °C (MeOH) (12%); IR 3370, 1734, 1690, 1668, 1625 cm^{-1}; ^1H NMR δ 1.45 (s, 9 H), 1.62 (s, 9 H), 2.10 (s, 6 H), 2.32 (s, 3 H), 3.70 (s, 3 H), 6.88 (s, 2 H). Anal. Calcd for $C_{23}H_{33}N_3O_3$: C, 69.17; H, 8.27; N, 10.52. Found: C, 69.27; H, 8.42; N, 10.58.

5-(*tert*-Butylamino)-2-(methylthio)-4-[(2,4,6-trimethylphenyl)(methoxycarbonyl)methylene]-4-isoimidazole (28): mp 170 °C (MeOH) (43%); IR 3410, 1714, 1643, 1564 cm^{-1}; ^1H NMR δ 1.50 (s, 9 H), 2.14 (s, 6 H), 2.34 (s, 6 H), 3.72 (s, 3 H), 6.92 (s, 2 H). Anal. Calcd for $C_{20}H_{27}N_3O_2S$: C, 64.34; H, 7.23; N, 11.26; S, 8.58. Found: C, 64.54; H, 7.40; N, 11.11; S, 8.53.

Cycloaddition Reactions of Diazatrienes with Isocyanides. To a solution of diazatriene **13**, **35**, or **36** (3 mmol) in dry THF or acetonitrile (15 mL) was added isocyanide (6 mmol). The mixture was heated at reflux under dry nitrogen for the time indicated in Table V. The solvent was evaporated and the residue was triturated with ether to give the imidazoline (or petroleum ether for imidazole **23**).

5-(*tert*-Butylimino)-4,4-dimethyl-2-(methylthio)-1-[2-(2,4,6-trimethylphenyl)-2-(methoxycarbonyl)vinyl]-2-imidazoline (20): mp 152 °C (MeOH); ^1H NMR δ 1.35 (s, 9 H), 1.45 (s, 6 H), 2.12 (s, 6 H), 2.22 (s, 3 H), 2.27 (s, 3 H), 3.72 (s, 3 H), 6.81 (s, 2 H), 7.52 (s, 1 H). Anal. Calcd for $C_{23}H_{33}N_3O_2S$: C, 66.50; H, 7.95; N, 10.12; S, 7.71. Found: C, 66.35; H, 7.98; N, 10.12; S, 7.52.

4,4-Dimethyl-2-(methylthio)-5-(isopropylimino)-1-[2-(2,4,6-trimethylphenyl)-2-(methoxycarbonyl)vinyl]-2-imidazoline (21): mp 124 °C (MeOH); IR 1706, 1670, 1614, 1567 cm^{-1}; ^1H NMR δ 0.85 (d, J = 6 Hz, 6 H), 1.35 (s, 6 H), 2.10 (s, 6 H), 2.24 (s, 3 H), 2.37 (s, 3 H), 3.71 (s, 3 H), 3.80 (m, J = 6 Hz, 1 H), 6.77 (s, 2 H), 7.47 (s, 1 H). Anal. Calcd for $C_{22}H_{31}N_3O_2S$: C, 65.83; H, 7.73; N, 10.47; S, 7.98. Found: C, 65.91; H, 7.81; N, 10.75; S, 8.10.

5-(*tert*-Butylimino)-4,4-diphenyl-2-(methylthio)-1-[2-(2,4,6-trimethylphenyl)-2-(methoxycarbonyl)vinyl]-2-imidazoline (22): mp 201 °C (MeOH); IR 1711, 1663, 1579, 1570 cm^{-1}; ^1H NMR δ 0.80 (s, 9 H), 2.12 (s, 6 H), 2.17 (s, 3 H), 2.27 (s, 3 H), 3.75 (s, 3 H), 6.82 (s, 2 H), 7.30 (s, 10 H), 7.72 (s, 1 H). Anal. Calcd for $C_{33}H_{37}N_3O_2S$: C, 73.47; H, 6.86; N, 7.79; S, 5.93. Found: C, 73.43; H, 6.82; N, 7.72; S, 6.10.

5-(*tert*-Butylamino)-2-(methylthio)-4-phenyl-1-[2-(2,4,6-trimethylphenyl)-2-(methoxycarbonyl)vinyl]imidazole (23): mp 145 °C (MeOH); IR 3358, 1712, 1628 cm^{-1}; ^1H NMR δ 0.85 (s, 9 H), 2.02 (s, 6 H), 2.31 (s, 3 H), 2.69 (s, 3 H), 3.81 (s, 3 H), 6.86 (s, 2 H), 7.2–7.8 (m, 5 H), 7.87 (s, 1 H). Anal. Calcd for $C_{27}H_{33}N_3O_2S$: C, 69.97; H, 7.12; N, 9.07; S, 6.91. Found: C, 70.09; H, 7.17; N, 9.09; S, 7.04.

2-[(5-(*tert*-Butylimino)-4,4-dimethyl-2-(methylthio)-2-imidazolin-1-yl)methylene]-3,3-diphenyl-*N*-methylsuccinimide (37): mp 160 °C (EtOH); ^1H NMR δ 1.28 (s, 6 H), 1.36 (s, 9 H), 1.99 (s, 3 H), 3.12 (s, 3 H), 7.3 (m, 10 H), 7.40 (s, 1 H). Anal. Calcd for $C_{28}H_{32}N_4O_2S$: C, 68.85; H, 6.55; N, 11.47; S, 6.55. Found: C, 68.73; H, 6.52; N, 11.26; S, 6.62.

2-[(4,4-Dimethyl-5-(isopropylimino)-2-(methylthio)-2-imidazolin-1-yl)methylene]-3,3-diphenyl-*N*-methylsuccinimide (38): mp 178 °C (MeOH); IR 1763, 1709, 1687, 1640, 1587 cm^{-1}; ^1H NMR (C_5D_5N) δ 0.84 (d, J = 6 Hz, 6 H), 1.20 (s, 6 H), 2.25 (s, 3 H), 2.90 (s, 3 H), 3.75 (m, J = 6 Hz, 1 H), 7.2–7.7 (m, 10 H), 7.53 (s, 1 H); ^{13}C NMR δ 178.0, 170.0, 162.6, 158.0, 137.5, 133.2, 130.3, 129.9, 127.9, 127.8, 67.6, 63.2, 48.9, 25.5, 24.2, 13.1. Anal. Calcd for $C_{27}H_{30}N_4O_2S$: C, 68.35; H, 6.32; N, 11.81; S, 6.75. Found: C, 68.14; H, 6.43; N, 11.86; S, 6.74.

2-[[4,4-Dimethyl-5-(diphenylmethylimino)-2-(methylthio)-2-imidazolin-1-yl]methylene]-3,3-diphenyl-*N*-methylsuccinimide (39): mp 184 °C (MeOH); ^1H NMR δ 1.22 (s, 6 H), 2.11 (s, 3 H), 3.11 (s, 3 H), 5.82 (s, 1 H), 7.3 (m, 20 H), 7.53 (s, 1 H). Anal. Calcd for $C_{37}H_{34}N_4O_2S$: C, 7.24; H, 5.68; N, 9.36; S, 5.35. Found: C, 74.12; H, 5.70; N, 9.40; S, 5.41.

2-[[5-(*tert*-Butylimino)-4,4-diphenyl-2-(methylthio)-2-imidazolin-1-yl]methylene]-3,3-diphenyl-*N*-methylsuccinimide (40): mp 213 °C (MeOH); ^1H NMR δ 0.90 (s, 9 H), 1.87 (s, 3 H), 3.17 (s, 3 H), 7.2 (m, 20 H), 7.62 (s, 1 H). Anal. Calcd for $C_{38}H_{36}N_4O_2S$: C, 74.50; H, 5.88; N, 9.15; S, 5.22. Found: C, 74.54; H, 5.87; N, 9.23, S, 5.14.

Thermolysis of Thioimidate 30. A solution of thioimidate **30** (2.1 g, 5 mmol) and *tert*-butyl isocyanide (0.8 g, 10 mmol) in MeCN (20 mL) was heated at reflux under nitrogen for 2 h. The reaction mixture was concentrated. The residue, according to ^1H NMR analysis, was a 1:1 mixture of **33** and **34**. These products were separated by addition of ether: **33** (22%), **34** (24%).

The thermolysis of **30** was also carried out in CH_2Cl_2 for 94 h. After workup of the reaction mixture in the usual way, ^1H NMR analysis showed a 1:3 mixture of **29** and **30**.

Registry No. **1a**, 70245-01-1; **1b**, 82940-34-9; **1c**, 82939-90-0;

1d, 82650-65-5; **1e**, 82650-66-6; **2** (R^1 = 4-MeC_6H_4, R^2 = Me, R^3 = *i*-Pr), 94518-47-5; **2** (R^1 = R^2 = Ph, R^3 = *i*-Pr), 94518-50-0; **2** (R^1 = $Ph_2C(CN)$, R^2 = CH_2Ph, R^3 = *i*-Pr), 94518-52-2; **2** (R^1 = $Ph_2C(CN)$, R^2 = Ph, R^3 = *i*-Pr), 94518-53-3; **2** (R^1 = $Ph_2C(CN)$, R^2 = Me, R^3 = *i*-Pr), 94518-54-4; **2** (R^1 = $Ph_2C(CN)$, R^2 = Me, R^3 = Ph_2CH), 94518-56-6; **3c**, 65739-14-2; **3j**, 94518-57-7; **3k**, 82650-31-5; **3l**, 94518-58-8; **3p**, 94518-59-9; **4**, 94518-60-2; **5**, 94518-61-3; **6**, 94518-62-4; **7**, 94518-63-5; **8**, 94518-64-6; **9**, 90496-26-7; **10c**, 94518-65-7; **10d**, 94518-66-8; **10g**, 94518-67-9; **10i**, 94518-68-0; **10j**, 94518-69-1; **10k**, 94518-70-4; (*E*)-**11a**, 94518-71-5; (*Z*)-**11a**, 94518-72-6; (*E*)-**11b**, 94518-73-7; (*Z*)-**11b**, 94518-74-8; **11j**, 94518-75-9; **12i**, 94518-76-0; **12o**, 94518-77-1; **12p**, 94518-78-2; **13c**, 94518-79-3; **13d**, 94518-80-6; **13e**, 94518-81-7; **13f**, 94518-82-8; **13g**, 94518-83-9; **13l**, 94518-84-0; **13m**, 94518-85-1; **13n**, 94518-86-2; **14c**, 94518-87-3; **14d**, 94518-88-4; **14e**, 94518-89-5; **14f**, 94518-90-8; **14g**, 94518-91-9; **14h**, 94518-92-0; **15**, 94518-93-1; **16**, 94518-94-2; **17**, 94518-95-3; **18**, 94518-96-4; **19**, 94518-97-5; **20**, 94518-98-6; **21**, 94518-99-7; **22**, 94519-00-3; **23**, 94519-01-4; **24**, 94519-02-5; **25**, 94519-03-6; **26**, 94519-04-7; **27**, 94519-05-8; **28**, 94519-06-9; **29**, 94519-07-0; **30**, 94519-08-1; **31**, 94519-09-2; **32**, 94519-10-5; **33**, 94519-11-6; **34**, 94519-12-7; **35**, 94519-13-8; **36**, 94519-14-9; **37**, 94519-15-0; **38**, 94519-16-1; **39**, 94519-17-2; **40**, 94519-18-3; *i*-PrNC, 598-45-8; Ph_2CHNC, 3128-85-6; 2,6-$Me_2C_6H_3NC$, 2769-71-3; *t*-BuNC, 7188-38-7.

A Nitrile Oxide Based Entry to 2,3-Dihydropyran-4-ones. Synthesis of a Protected Version of "Compactin Lactone" in Racemic and Optically Active Forms

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The use of nitrile oxides bearing a masked β-oxo group as β-hydroxy-3-oxopropionylating agents for the vicinal functionalization of olefins is described. The β-hydroxy ketones revealed on hydrogenation of the initially formed 1,3-dipolar cycloaddition products undergo zinc triflate promoted cyclocondensation to 2,3-dihydropyran-4-ones, useful carbohydrate building blocks. The application of this chemistry to the preparation of a protected form of "compactin lactone" is detailed.

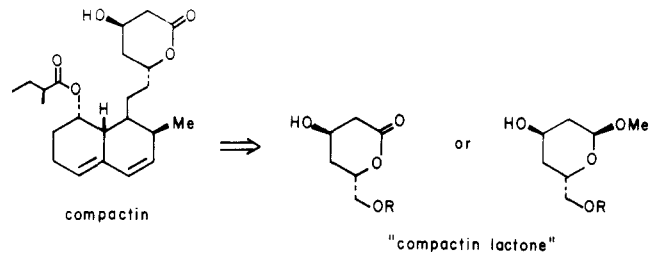
The de novo synthesis of carbohydrates and carbohydrate-related materials has long been of interest to many investigators.[1] While the Diels–Alder reaction of carbonyl dienophiles with oxygenated dienes has proven popular both in the past and the present,[1,2] it does have in spite of its successes some obvious shortcomings.

In further pursing our interests in this area[3] we have had the occasion to develop a 1,3-dipolar cycloaddition based entry to the important carbohydrate building blocks, the 2,3-dihydropyran-4-ones. The evolution of this work in the context of developing a synthesis approach to a protected form of compactin lactone is detailed herein.

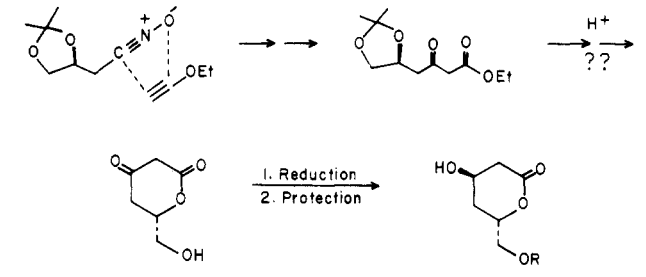
Synthesis of Compactin Lactone, Preliminary Studies

In devising an approach to compactin lactone (this lactone and a protected version of it are shown in Scheme I), we focused initially on the strategy shown in Scheme II. (*R*)-2,3-Isopropylideneglyceraldehyde[4] was transformed to the nitro compound **2** via a Henry reaction/reduction sequence,[5] and **2** reacted with phenyl isocyanate/triethylamine in the presence of ethoxyacetylene[3d] to yield isoxazole **3** (Scheme III). While hydrogenation delivered the β-keto ester **4** cleanly, subsequent *p*-toluenesulfonic acid treatment of this intermediate led either to a complicated mixture of products containing some of the diol **5** (MeOH, room temperature) or to the furan **6** as a mixture of methyl and ethyl esters by dehydrative cyclization. None of the desired cyclized lactone was observed. Additionally, attempts to either protect or to reduce the ketone group of **4** and then to effect cyclization were disappointing.

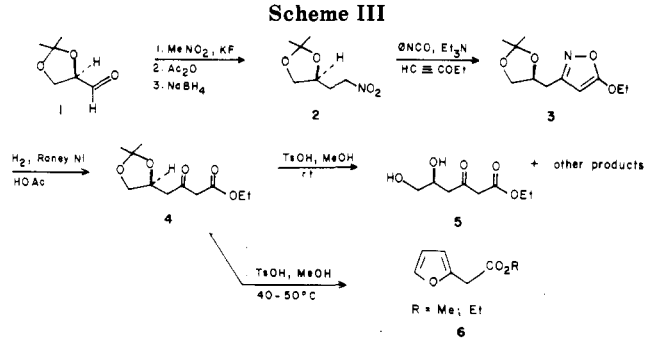
Scheme I



Scheme II



Scheme III



Furthermore, the nitrile oxide derived from **2** was added to vinyl bromide[6] to form the isoxazole **7**. The acetonide

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