Regioselective Cycloadditions of N-Protonated Azomethine Ylides and 2-Azaallyl Anions Generated from *N*-(Silylmethyl) Thioimidates, Synthetic Equivalents of Nonstabilized Nitrile Ylides

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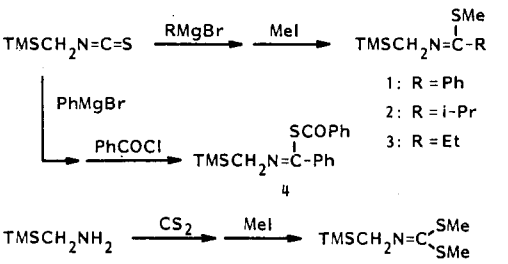
A water-induced-desilylation method and a direct-desilylation method have been applied to *N*-(silylmethyl) thioimidates to lead to the generation of N-protonated azomethine ylides and 2-azaallyl anions, respectively. These reactive intermediates are captured as cycloadducts to electron-deficient olefins, aldehydes, and ketones. The reactions with unsymmetrically substituted olefins are highly regioselective but with reverse selectivity. Regioisomeric 1-pyrrolines are accessible through the two desilylation methods on the same thioimidates.

Since the pioneering work by Vedejs and Martinez in 1979 on a new method for generating nonstabilized nitrogen, sulfur, and phosphorus methylides,[1] numerous reports have appeared that deal with a variety of the desilylation methods of *N*-(silylmethyl) imines and related compounds for the generation of azomethine ylides.[2-5] Some of these methods have been successfully applied to natural product synthesis.[6]

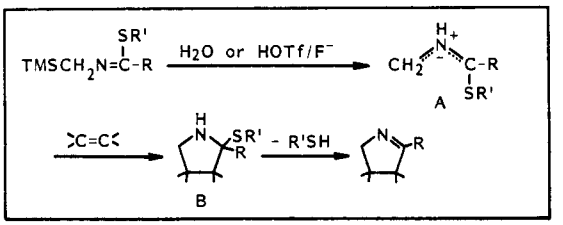
Water-induced desilylation of *N*-(silylmethyl) imines[7,8] and fluoride-mediated desilylation after the in situ S- or N′-alkylation of *N*-(silylmethyl) thioimides[9] (or amidines[9,10]) are synthetically valuable since they can lead to novel 1,3-dipoles, N-protonated azomethine ylides.[11] *N*-(Silylmethyl) imines can be desilylated also directly, without quarternization at the imine nitrogen, to generate 2-azaallyl anions, which undergo Michael addition to electron-deficient olefins.[8]

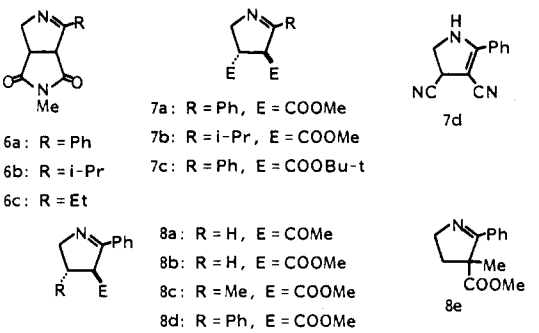
In the present article, both the water-induced desilylation method and the direct desilylation method[12] have been extended to *N*-(silylmethyl) thioimidates.[13] Generation of both N-protonated azomethine ylides and 2-azaallyl anions is expected. The alkylthio moiety will facilitate the desilylation through its capability of stabilizing the anionic centers, and it will also serve as a leaving group so that these ylides as well as the anions will be the synthons for nitrile ylides.

Scheme I



Scheme II





Results and Discussion

N-(Silylmethyl) thioimidates 1–4 were readily prepared by the S-methylation or -benzoylation of *N*-(silylmethyl) thioamides whose preparation by the addition of Grignard

(1) Vedejs, E.; Martinez, G. R. *J. Am. Chem. Soc.* **1979**, *101*, 6452.
(2) From *N*-(silylmethyl) imines: (a) Achiwa, K.; Sekiya, M. *Chem. Lett.* **1981**, 1213 and **1982**, 2589. (b) Livinghouse, T.; Smith, R. *J. Chem. Soc., Chem. Commun.* **1983**, 210. (c) Achiwa, K.; Motoyoma, T.; Sekiya, M. *Chem. Pharm. Bull.* **1983**, *31*, 3939. (d) Achiwa, K.; Imai, N.; Motoyama, T.; Sekiya, M. *Chem. Lett.* **1984**, 2041. (e) Achiwa, K.; Imai, N.; Inaoka, T.; Sekiya, M. *Chem. Pharm. Bull.* **1984**, *32*, 2878. (f) Imai, N.; Terao, Y.; Achiwa, K. *Heterocycles* **1985**, *23*, 1107. (g) Achiwa, K.; Sugiyama, K.; Sekiya, M. *Chem. Pharm. Bull.* **1985**, *33*, 1975.
(3) From *N*-silylmethylation: (a) Terao, Y.; Imai, N.; Achiwa, K.; Sekiya, M. *Chem. Pharm. Bull.* **1982**, *30*, 3167. (b) Padwa, A.; Hafmanns, G.; Tomas, M. *Tetrahedron Lett.* **1983**, *24*, 4303. (c) Padwa, A.; Haffmanns, G.; Tomas, M. *J. Org. Chem.* **1984**, *49*, 3314.
(4) From *N*-(silylmethyl) amides or *N*-(silylmethyl) thioamides: Vedejs, E.; West, F. G. *J. Org. Chem.* **1983**, *48*, 4773.
(5) From silylmethylamines: (a) Padwa, A.; Chen, Y.-Y. *Tetrahedron Lett.* **1983**, *24*, 3447. (b) Hosomi, A.; Sakata, Y.; Sakurai, H. *Chem. Lett.* **1984**, 1117. (c) Terao, Y.; Kotani, H.; Imai, N.; Achiwa, K. *Chem. Pharm. Bull.* **1985**, *33*, 2762. (d) Padwa, A.; Chen, Y.-Y.; Chiacchio, U.; Dent, W. *Tetrahedron* **1985**, *41*, 3529. (e) Padwa, A.; Chen, Y.-Y.; Dent, W.; Nimmesgern, H. *J. Org. Chem.* **1985**, *50*, 4006.
(6) (a) Vedejs, E.; Martinez, G. R. *J. Am. Chem. Soc.* **1980**, *102*, 7993. (b) Smith, R.; Livinghouse, T. *J. Org. Chem.* **1983**, *48*, 1554. (c) Vedejs, E.; Larsen, S.; West, F. G. *J. Org. Chem.* **1985**, *50*, 2170. (d) Smith, R.; Livinghouse, T. *Tetrahedron* **1985**, *41*, 3559.
(7) Tsuge, O.; Kanemasa, S.; Hatada, A.; Matsuda, K. *Chem. Lett.* **1984**, *801*.
(8) Tsuge, O.; Kanemasa, M.; Hatada, A.; Matsuda, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2537.
(9) Tsuge, O.; Kanemasa, S.; Matsuda, K. *J. Org. Chem.* **1986**, *51*, 1997.
(10) Tsuge, O.; Kanemasa, K.; Matsuda, K. *Chem. Lett.* **1985**, 1411.
(11) For the other routes to N-protonated azomethine ylides, see: (a) Grigg, R.; Kemp, J. *J. Chem. Soc., Chem. Commun.* **1978**, 109. (b) Joucla, M.; Hamelin, J. *Tetrahedron Lett.* **1978**, 2885. (c) Tsuge, O.; Ueno, K.; Oe, K. *Chem. Lett.* **1979**, *1407*. (d) Grigg, R. *Bull. Soc. Chim. Belg.* **1984**, *93*, 593. (e) Joucla, M.; Mortier, J. *J. Chem. Soc., Chem. Commun.* **1985**, 1566. (f) Tsuge, O.; Kanemasa, S.; Ohe, M.; Takenaka, S. *Chem. Lett.* **1986**, 973.
(12) Reference 8 describes the first generation of nonstabilized 2-azaallyl anions by the direct desilylation of *N*-(silylmethyl) imines.
(13) Water-induced desilylation of *N*-(silylmethyl) thioimidates has been already reported as a preliminary communication: Tsuge, O.; Kanemasa, S.; Yamada, T.; Matsuda, K. *Heterocycles* **1985**, *23*, 2489.

0022-3263/87/1952-2523$01.50/0

Table I. Cycloaddition of N-Protonated Azomethine Ylides A Generated from *N*-[(Trimethylsilyl)methyl] Thioimidates 1–4

dipolarophile	ylide precursor	reaction conditions[a] solvent[c]	promotor[d]	temp,[e] °C	time, h	product	yield,[b] %
N-methylmaleimide	1	HMPA	W	rt	24	**6a**	98
	1	DME	TA–CsF	rt	13	**6a**	87
	4	HMPA	W–AA	60	36	**6a**	70
	2	HMPA	W	rt	24	**6b**	23
	2	AN	TA–CsF	rt	13	**6b**	81
	3	HMPA	W	rt	24	**6c**	10
dimethyl fumarate	1	HMPA	W	rt	24	**7a**	80
	2	HMPA	W–AA	rt	24	**7b**	23
dimethyl maleate	1	HMPA	W	rt	24	**7a**	62
di-*tert*-butyl fumarate	1	HMPA	W	rt	24	**7c**	70
di-*tert*-butyl maleate	1	HMPA	W	rt	24	**7c**	62
fumaronitrile	1	HMPA	W	rt	24	**7d**	77
3-buten-2-one	1	HMPA	W	rt	24	**8a**	75
	1	DME	TA–CsF	rt	13	**8a**	25
methyl acrylate	1	HMPA	W	rt	24	**8b**	62
methyl crotonate	1	HMPA	W	rt	24	**8c**	68
methyl cinnamate	1	HMPA	W	rt	24	**8d**	75
methyl methacrylate	1	HMPA	W	rt	24	**8e**	71

[a] Equimolar amounts of *N*-(silylmethyl) thioimidates and dipolarophiles were used in all reactions. [b] All isolated yields. [c] HMPA, hexamethylphosphoric triamide; DME, 1,2-dimethoxyethane; AN, acetonitrile. [d] W, water; TA, trifluoromethanesulfonic acid; AA, acetic acid. All promoters were used in equimolar amounts to the substrates. [e] Room temperature, rt.

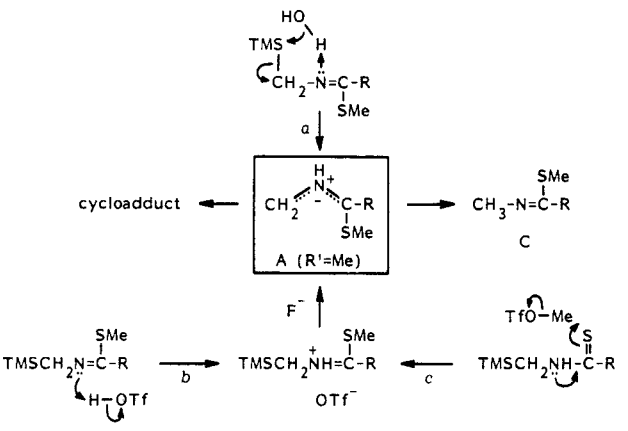
reagents to (trimethylsilyl)methyl isothiocyanate was already reported (Scheme I).[16] Both the Grignard addition and the S-methylation (or S-benzoylation) could be simply carried out in the same flask. Thus, *N*-(silylmethyl) thioimidates bearing a variety of substituents on the thioimidate carbon and sulfur were available.[17]

N-(Silylmethyl) bis(methylthio) imine **5**, bearing two anion-stabilizing methylthio moieties, was prepared by the reaction of [(trimethylsilyl)methyl]amine with carbon disulfide followed by methylation with 2 equiv of methyl iodide.

Water-Induced Desilylation of *N*-(Silylmethyl) Thioimidates Leading to N-Protonated Azomethine Ylides and Cycloadditions with Olefinic Dipolarophiles. *N*-(Silylmethyl) thioimidate **1** was first subjected to the usual methods for generating azomethine ylides from *N*-(silylmethyl) imines, which include the initial silylation or acylation at the imine nitrogen and the subsequent desilylation.[2] When **1** was treated either with trimethylsilyl triflate and cesium fluoride in HMPA or with benzoyl fluoride in acetonitrile, only fair yields of the corresponding azomethine ylides were generated.[18]

Treatment of **1** and *N*-methylmaleimide with water in HMPA at room temperature afforded a quantitative yield of 2-methyl-4-phenyl-1,2,3,3a,6,6a-hexahydropyrrolo[3,4-*c*]pyrrole-1,3-dione (**6a**) (Scheme II and Table I). Thus, the water-induced-desilylation method worked effectively, generating N-protonated azomethine ylide A (R = Ph, R′ = Me), which survived under aqueous conditions. Ylide A reacted with *N*-methylmaleimide prior to its tautomerization into the *N*-methyl thioimidate. The resulting cycloadduct B underwent elimination of thiol to give **6a**, which corresponds to a formal cycloadduct of a nonstabilized nitrile ylide.[19]

Scheme III



More *N*-(silylmethyl) thioimidates and olefinic dipolarophiles were employed in order to know the scope and limitation of the water-induced-desilylation method.

N-(Silylmethyl) thioimidate **1**, bearing a phenyl group at the thioimidate carbon, reacted smoothly with olefinic dipolarophiles under similar conditions to give thiol-eliminated cycloadducts **6–8** (Scheme II and Table I). Exclusive formation of 3,4-*trans*-1-pyrroline **7a** (or **7c**) from both dimethyl (or di-*tert*-butyl) fumarate and maleate is due to a ready imine/enamine tautomerism (or a 1-pyrroline-/2-pyrroline isomerization).[9,15b]

Cycloadditions of A (R = Ph, R′ = Me) to unsymmetrically substituted olefins furnished exclusively the 1-pyrrolines **8a–e** with an electron-withdrawing substituent at the 3-position (Scheme II and Table I). This regioselectivity resembles that of simple azomethine ylides of nonstabilized type,[7,8] and accordingly the present cycloaddition presumably proceeded under the control of a $HOMO_{1,3\text{-dipole}}$–$LUMO_{dipolarophile}$ interaction.[20]

Structural assignment of these cycloadducts was based on spectral data as well as elemental analyses. The re-

(14) Several sulfur-stabilized azomethine ylides are known. See refs 3b,c, 4, and 6b,d.

(15) (a) Tsuge, O.; Kanemasa, S.; Yorozu, K.; Ueno, K. *Chem. Lett.* **1985**, 1601. (b) Tsuge, O.; Ueno, K.; Kanemasa, S.; Yorozu, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1809.

(16) (a) Tsuge, O.; Kanemasa, S.; Matsuda, K. *Chem. Lett.* **1983**, 1131. (b) Tsuge, O.; Kanemasa, S.; Matsuda, K. *J. Org. Chem.* **1984**, *49*, 2688.

(17) Methyl, butyl, and vinyl moieties could be introduced as well by similar reactions employing the corresponding Grignard reagents.

(18) Azomethine ylides generated from **1** were captured by *N*-methylmaleimide as the same cycloadduct **6a**: 25% after 16 h at 60 °C in HMPA in the presence of Me_3SiOTf and CsF; 44% after 16 h at 60 °C in MeCN in the presence of PhCOF.

(19) Thiol elimination of cycloadduct B was completed during the chromatographic operation of crude products, indicating that N-protonated azomethine ylides A, not nitrile ylides, were involved in the reaction.

(20) Imai, N.; Tokiwa, H.; Akahori, Y.; Achiwa, K. *Chem. Lett.* **1986**, 1113.

giochemistry was determined by the comparison of ^1H and ^{13}C NMR data of two regioisomeric cycloadducts (e.g., **8e** vs. **11a**). This will be discussed later.

The azomethine ylides A (R = Et, *i*-Pr; R′ = Me) generated from alkyl-substituted thioimidates **2** and **3** are inactive. Only highly activated olefins such as *N*-methylmaleimide and dimethyl fumarate can react with A, but the yields of cycloadducts (**6b**, **6c**, and **7b**) were extremely low. Major products in these cases were *N*-methylthioimidates C as tautomers of N-protonated azomethine ylides A (Scheme III). Thus, ylides A undergo an irreversible 1,2-proton migration into C if the reactivity of either dipolarophiles or ylides is not sufficient.

In the water-induced-desilylation method, as much as 5 equiv of water can be used without any serious trouble so that the reaction may be carried out in commercially available wet HMPA.[21] Noteworthy are the following: (1) Water acts efficaciously not only as a promoter in the ylide generation but also as an inhibitor in the undesired polymerization of electron-deficient olefins.[22] (2) N-Protonated azomethine ylides A are stabilized by the alkylthio substituent enough to undergo clean 1,3-dipolar cycloadditions under the conditions of ylide generation. (3) Cycloadducts B quickly eliminate the sulfur substituent, leading to formal cycloadducts of nitrile methylides. (4) These reactions can be performed in a single simple operation under mild reaction conditions.[23]

We have previously reported the generation of N-protonated azomethine ylides A (R = Ph, Et; R′ = Me) by S-methylation of the corresponding *N*-(silylmethyl) thioamides with methyl triflate and subsequent desilylation (route c, Scheme III).[9] When the results obtained from routes a and c are compared, it is immediately realized that reactivity of the ylides A depends upon the conditions of generation. Yields of cycloadducts are equally good regardless of substituent R when the yields A are generated from route c. On the other hand, alkyl-substituted ylides A (R = alkyl) are rather sluggish when generated by the water-induced-desilylation method.

It is expected that the intermediate salts from route c will be also available by N-protonation of *N*-(silylmethyl) thioimidates with triflic acid. Thus, thioimidates **1** and **2** were protonated with triflic acid (TfOH) in DME and then desilylated with cesium fluoride.[24] The N-protonated azomethine ylides A (R = Ph, *i*-Pr; R′ = Me) generated were trapped with olefins. The yield of cycloadduct **6b** of an alkyl-substituted ylide (A: R = *i*-Pr; R′ = Me) with *N*-methylmaleimide was improved (this method, 81%; the water method, 23%).[25]

Fluoride-Induced Desilylation of *N*-(Silylmethyl) Thioimidates Leading to 2-Azaallyl Anions and Cycloadditions with Olefins or Carbonyl Compounds. Desilylation of *N*-(silylmethyl) thioimidates without quaternization at the thioimidate nitrogen generates 2-azaallyl anions D (Scheme IV). Although azomethine ylides and 2-azaallyl anions are isoelectronic with the only difference being occupancy of the nonbonding electron pair on the nitrogen, they show different chemical properties. They

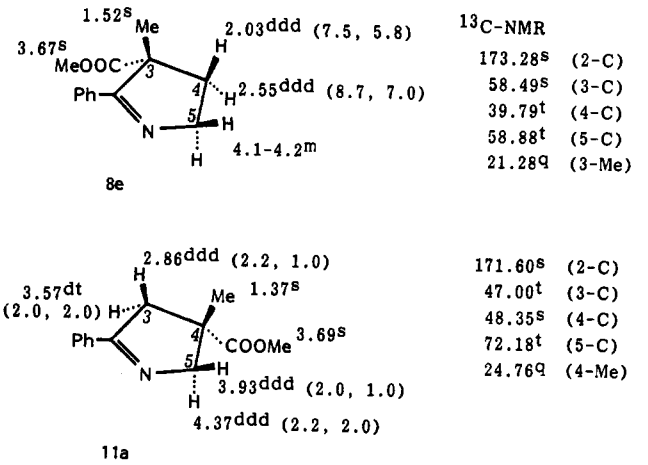
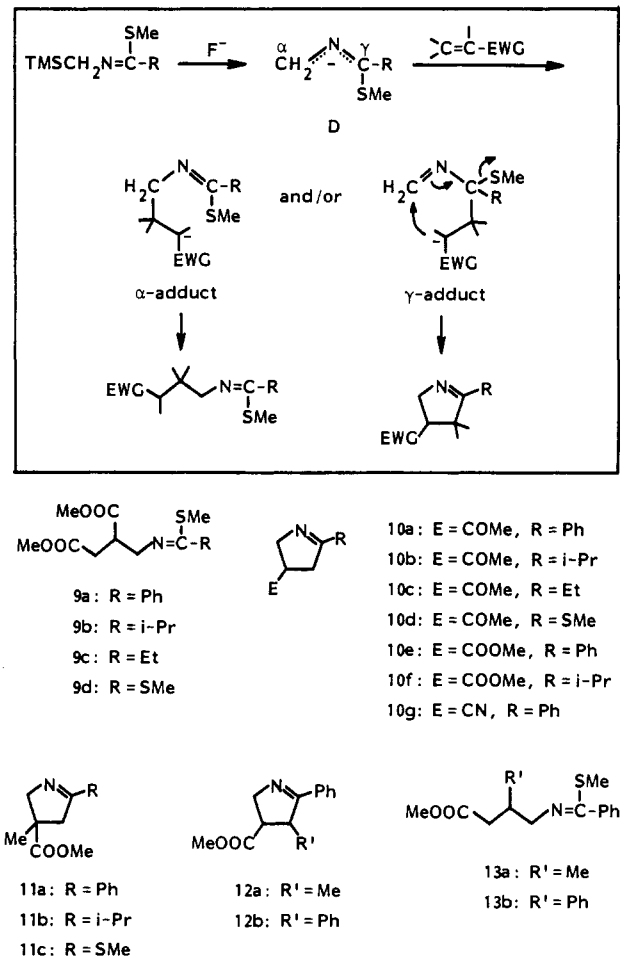


Figure 1. ^1H and ^{13}C NMR spectral data (chemical shift, δ; coupling, Hz) of regioisomeric cycloadducts **8e** and **11a**.

Scheme IV



are therefore complementary in organic synthesis. Our recent report might be the only one that has demonstrated the generation of both azomethine ylides and 2-azaallyl anions from the same imines.[8]

N-(Silylmethyl) thioimidate **1** was treated with a catalytic amount of tetrabutylammonium fluoride (TBAF, 10 mol %) in THF. The 2-azaallyl anion D (R = Ph) generated was captured with methyl fumarate or maleate to give the same Michael adduct **9a**. It was assigned to be the adduct formed by an attack of the α-carbon of D (Scheme IV). Similarly, 2-azaallyl anions D (R = Et, *i*-Pr, SMe) generated from *N*-(silylmethyl) imines **2** and **3**, and *N*-(silylmethyl) bis(methylthio) imine **5** reacted with

(21) Reaction of **1** with *N*-methylmaleimide was examined. When more than 5 equiv of water was present, the yield of **6a** decreased and a comparable amount of methyl *N*-methylbenzene thioimidate C (R = Ph) was present.

(22) The polymerization of electron-deficient activated olefins in highly dry HMPA has been already discussed (refs 7 and 8).

(23) The meaning of "mild" is that this reaction can be carried out at room temperature and in wet solvent.

(24) Use of dry hydrogen chloride instead of HOTf failed in the generation of ylides A, *N*-methyl thioimidates C being the major products.

(25) Ylide A (R = *i*-Pr; R′ = Me) was still inactive with methyl acrylate, acrylonitrile, or 3-buten-2-one, no cycloadducts being obtained.

Table II. Reaction of 2-Azaallyl Anions D Generated by Desilylation of *N*-[(Trimethylsilyl)methyl] Thioimidates 1–4 or *N*-[(Trimethylsilyl)methyl] Bis(methylthio) Imine 5 with Tetrabutylammonium Fluoride

Michael acceptor	2-azaallyl anion precursor	reaction temp and time[a]	product	yield,[b] %
dimethyl fumarate	1	rt,[e] 4 h	**9a**	80
	2	0 °C, 1.5 h, then rt, 6 h	**9b**	62
	3	0 °C, 0.5 h, then rt, 6 h	**9c**	48
	5	0 °C, 1 h, then rt, 7 h	**9d**	61
dimethyl maleate	1	0 °C, 0.5 h, then rt, 4 h	**9a**	71
3-buten-2-one	1	0 °C, 6 h	**10a**	74
	2	−15 °C, 1.5 h, then rt, 6 h	**10b**	57
	3	0 °C, 0.5 h, then rt, 6 h	**10c**	48
	5	−15 °C, 0.5 h, then rt, 6 h	**10d**	58
methyl acrylate	1	0 °C, 0.5 h, then rt, 4 h	**10e**	74
	2	0 °C, 1.5 h, then rt, 6 h	**10f**	55
acrylonitrile	1	0 °C, 0.5 h, then rt, 4 h	**10g**	72
methyl methacrylate	1	0 °C, 0.5 h, then rt, 4 h	**11a**	75
	2	−15 °C, 1.5 h, then rt, 6 h	**11b**	52
	5	−15 °C, 1.5 h, then rt, 5 h	**11c**	45
methyl crotonate	1	0 °C, 0.5 h, then rt, 4 h	**12a** + **13a**[c]	63
methyl cinnamate	1	0 °C, 0.5 h, then rt, 4 h	**12b** + **13b**[d]	75

[a] All reactions were carried out in dry THF under nitrogen in the presence of 10 mol % of TBAF. Equimolar amounts of thioimidates and olefins were used. [b] All isolated yields. [c] **12a**:**13a** = 24:76 (by GLC). [d] **12b**:**13b** = 19:81 (by GLC). [e] Room temperature, rt.

Table III. Optimization of the Reactions of 2-Azaallyl Anions D with Unsymmetrically Substituted Olefinic Acceptors

Michael acceptor	anion precursor	solvent[a]	TBAF, equiv	reaction temp and time	product	yield,[b] %
methyl methacrylate	1	THF	0.1	rt,[c] 4 h	**11a**	59
		THF	0.05	rt, 4 h	**11a**	50
		DMF	0.1	rt, 4 h	**11a**	44
		AN	0.1	rt, 4 h	**11a**	31
		THF	0.1	−15 °C, 4 h	**11a**	30
		THF	0.1	0 °C, 0.5 h, then rt, 4 h	**11a**	77
	2	THF	0.1	−15 °C, 1.5 h, then rt, 6 h	**11b**	54
		DMF	0.1	−15 °C, 1.5 h, then rt, 6 h	**11b**	50
3-buten-2-one	2	THF	0.1	0 °C, 0.5 h, then rt, 9 h	**10b**	42
		THF	0.1	−15 °C, 0.5 h, then rt, 6 h	**10b**	60
	5	THF	0.1	0 °C, 0.5 h, then rt, 4 h	**10d**	12
		THF	0.1	−15 °C, 0.5 h, then rt, 5 h	**10d**	61

[a] DMF, dimethylformamide; AN, acetonitrile. [b] Based on GLC analysis of the crude reaction mixtures. [c] Room temperature, rt.

methyl fumarate to give regioselective Michael adducts **9b–d** (Table II).

On the other hand, reactions of D with monosubstituted olefins such as 3-buten-2-one, methyl acrylate, and acrylonitrile or a 1,1-disubstituted olefin such as methyl methacrylate afforded 1-pyrrolines **10a–g** or **11a–c**, respectively, as sole products (Table II). Interestingly, these 1-pyrrolines **10** and **11** are regioisomers of **8**, which were exclusively produced in the aforementioned cycloadditions of N-protonated azomethine ylides A (see Scheme II).

^1H and ^{13}C NMR spectral data of regioisomeric cycloadducts **8e** and **11a** are shown in Figure 1. An isomer **8e**, which bears two adjacent methylenes, was assigned to be methyl 3-methyl-2-phenyl-1-pyrroline-3-carboxylate, while **11a**, bearing two separated methylenes, was assigned as methyl 4-methyl-2-phenyl-1-pyrroline-4-carboxylate. A high-field triplet at 39.79 ppm is assigned to the unsubstituted 4-C of **8e**, and a low-field triplet for 5-C of **11a** (72.18 ppm; 5-C of **8e**, 58.88 ppm) is due to high substitution at the adjacent 4-position. Other 1-pyrrolines **10** and **11** were similarly assigned by comparison of spectral data with those of **8**.

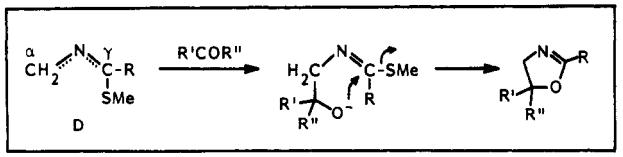
As mentioned above, reactions of 2-azaallyl anions D with olefin acceptors led to two types of products, Michael adducts **9** and 1-pyrrolines **10** and **11** (Scheme IV). The reaction initiated at the α-carbon of D led to Michael adducts and, at the γ-carbon, 1-pyrrolines. The reaction site of D is determined by the steric size of acceptors. The initial reaction occurs at the less hindered α-carbon when the electrophilic carbon of olefins is substituted by a bulky group. Consequently the imine carbon of the intermediary adduct is sterically hindered so that no cyclization takes place. When the β-carbon of olefins is unsubstituted, D reacts at the γ-carbon where an anion is more highly stabilized. Subsequent cyclization is easy because of the absence of serious steric repulsion.

This interpretation was confirmed by the reaction of D with other β-substituted Michael acceptors. Reaction of D (R = Ph) with methyl crotonate or cinnamate afforded a 24:76 mixture of 1-pyrroline **12a** and Michael adduct **13a** or a 19:81 mixture of **12b** and **13b**, respectively (Scheme IV and Table II).

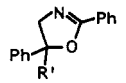
Some important information was obtained from the reactions of 2-azaallyl anions D with methyl methacrylate or 3-buten-2-one under various conditions (Table III): (1) A catalytic amount (10 mol %) of TBAF was sufficient. Use of 1 equiv resulted in the formation of a complex mixture of products. (2) Compared to the 2-azaallyl anions derived from *N*-benzylidene [(trimethylsilyl)methyl]-amine,[7,8] anions D are highly stabilized. No polymerization of olefin acceptors was observed in the absence of water, and smooth Michael addition occurred even in dry THF.[26] (3) Alkyl-substituted thioimidates **2** and **3** can be desilylated also. (4) Better yields of **10** and **11** were obtained when TBAF was slowly introduced to a cooled mixture of the substrates (0 to −15 °C) and the initial stage of reaction

(26) No desilylation occurred on treatment of *N*-benzylidene[(trimethylsilyl)methyl]amine with TBAF in THF. HMPA or DMF was needed as an anion-stabilizing solvent. The anion generated in such a polar solvent caused ready polymerization of the olefins which have been added to capture the anionic species (refs 7 and 8).

Scheme V



14a: Ar = R = Ph
14b: Ar = Ph, R = i-Pr
14c: Ar = Ph, R = Et
14d: Ar = 2-pyridyl, R = Ph



15a: R' = Ph
15b: R' = Me

Table IV. Reaction of 2-Azaallyl Anions D with Aldehydes or Ketones

carbonyl compound[a]	anion precursor	conditions[b,c]	product	yield,[d] %
benzaldehyde	1	rt, 7 h	**14a**	82
	2	70 °C, 12 h	**14b**	45
	3	70 °C, 10 h	**14c**	43
pyridine-2-carbaldehyde	1	rt, 12 h	**14d**	78
benzophenone	1	rt, 12 h	**15a**	72
acetophenone	1	rt, 7 h	**15b**	85

[a] Two equimolar amounts of carbonyl compounds were used. [b] All reactions were carried out in dry THF under nitrogen in the presence of TBAF (10 mol %). [c] Room temperature, rt. [d] All isolated yields based on the anion precursors.

was performed also at low temperature.

As shown in Scheme V, 2-azaallyl anions D generated under similar conditions reacted with aromatic aldehydes to give 2,5-disubstituted 2-oxazolines **14** (Table IV). In these cases also, the sterically crowded carbonyl carbon was attacked by the sterically less hindered α-carbon of D. Although less reactive benzophenone and enolizable acetophenone smoothly reacted with D, affording the corresponding 2-oxazolines **15**, all reactions with aliphatic aldehydes and ketones were unsuccessful. *N*-Methyl thioimidates (C in Scheme III) as protodesilylated products of *N*-(silylmethyl) thioimidates were obtained.

It is quite recently that Turro et al. have reported the direct generation of nitrile ylides by a similar combination of reagents.[27] They treated phenyl *N*-[(trimethylsilyl)-methyl]ethanethioimidate with silver fluoride in acetonitrile at 25 °C, and the species generated were trapped with olefins such as fumaronitrile, acrylonitrile, and methyl acrylate. Their 1-pyrrolines as nitrile ylide cycloadducts have different regiochemistry from ours. We assume that 2-azaallyl anions could have been generated in their case also, however, the countercation (Ag^+) would have abstracted the phenylthio moiety immediately after the anion formation leading to nitrile ylides.

It is concluded that *N*-(silylmethyl) thioimidates **1–5** are versatile reagents in heterocyclic synthesis because they can serve as common precursors for novel N-protonated azomethine ylides A and for 2-azaallyl anions D. These two active species are synthetic equivalents of nonstabilized nitrile ylides, and further they show opposite regioselectivity in cycloadditions.

Experimental Section

General. Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were taken with a JASCO IRA-1 or a JASCO A-702 spectrometer. ^1H NMR spectra were recorded on a Hitachi R-40 (90 MHz) or a JEOL FX-100 instrument (100 MHz) and ^{13}C NMR on a JOEL FX-100 spectrometer at 25.05 MHz. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Mass spectra were measured with a JEOL-01SG-2 spectrometer at 70 eV of ionization energy. Elemental analyses were performed on a Hitachi 026 CHN analyzer. Thin-layer chromatography (TLC) was accomplished on 0.2-mm precoated plates of silica gel 60 F-254 (Merck) or of aluminum oxide 60 F-254 type E (Merck). Visualization was made with ultraviolet light (254 and 365 nm), iodine, molybdophosphoric acid (5% in ethanol), or *p*-anisaldehyde (5% in ethanol containing 5% of sulfuric acid). For preparative column chromatography, Wakogel C-200, C-300 (Wako), and silica gel 60 (Merck) were employed. Flash chromatography was carried out on an EYELA EF-10 apparatus using a column (20 × 180 mm) packed with silica gel 60 (Merck, 0.04–0.063 mm). Gas–liquid chromatography (GLC) was accomplished on a Yanaco G-2800 gas chromatograph (Yanagimoto) with an ionization flame detector using a glass column (SE-30, 3 × 2000 mm) or a glass capillary column (silicone GE, SE-30, 0.25 × 5000 mm). Micro vacuum distillation was carried out on a Sibata GTO-250R Kugelrohr distilling apparatus. Solvents were evaporated with a Tokyo Rikakikai rotary evaporator type V at about 50 °C unless otherwise stated.

Solvents and Materials. Acetonitrile (AN), 1,2-dimethoxyethane (DME), and tetrahydrofuran (THF) were distilled from P_2O_5, CaH_2, and $LiAlH_4$, respectively, immediately prior to their use. Dimethylformamide (DMF) and hexamethylphosphoric triamide (HMPA) were distilled under vacuum and stored over 5A molecular sieves. Cesium fluoride was dried under vacuum prior to its use. Tetrabutylammonium fluoride (1 M solution in THF) was dried over 5A molecular sieves. Trifluoromethanesulfonic acid is commercially available. (Trimethylsilyl)methyl isothiocyanate,[16] (trimethylsilyl)methylamine,[8] and *N*-[(trimethylsilyl)methyl]thiobenzamide[9] were all prepared according to the known methods.

General Procedure for the Preparation of *N*-(Silylmethyl) Thioimidates 1–3. To a solution of phenyl- or alkylmagnesium bromides (11 mmol) freshly prepared in dry THF (30 mL) was added at room temperature (trimethylsilyl)methyl isothiocyanate (1.45 g, 10 mmol), and the mixture was stirred under nitrogen at room temperature for 1.5 h. After methyl iodide (1.56 g, 11 mmol) was added at 0 °C, the mixture was stirred at room temperature for 16 h, diluted with diethyl ether (100 mL), and then washed with water (100 mL × 2). The organic layer was dried over magnesium sulfate and evaporated in vacuo. The residue was distilled under vacuum on a Kugelrohr apparatus.

1 (mixture of *E* and *Z* isomers (*E*:*Z* = 1:3)): colorless liquid; bp 110 °C (2 mmHg) (bulb to bulb); IR (neat) 1610, 1595, 1245, and 855 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (2.25 H, s, Me_3Si), 0.19 (6.75 H, s, Me_3Si), 2.20 (2.25 H, s, SMe), 2.35 (0.75 H, s, SMe), 3.15 (0.5 H, s, CH_2SiMe_3), 3.60 (1.5 H, s, CH_2SiMe_3), and 7.1–7.4 (5 H, m, Ph); MS, *m/z* (relative intensity) 237 (M^+, 38), 236 (27), 190 (55), 121 (31), 118 (27), 117 (base peak), 87 (44), and 73 (33). Anal. Calcd for $C_{12}H_{19}NSSi$: C, 60.70; H, 8.07; N, 5.89. Found: C, 60.65; H, 8.16; N, 5.90.

2 (mixture of *E* and *Z* isomers (*E*:*Z* = 5:2)): colorless liquid; bp 70 °C (0.3 mmHg) (bulb to bulb); IR (neat) 1620, 1245, and 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.12 (9 H, s, Me_3Si), 1.13 (6 H, d, Me of *i*-Pr), 2.15 (0.86 H, s, SMe), 2.37 (2.14 H, s, SMe), 2.82 (1 H, m, CH of *i*-Pr), 3.22 (0.57 H, s, CH_2SiMe_3), and 3.30 (1.43 H, s, CH_2SiMe_3); MS, *m/z* (relative intenstiy) 203 (M^+, 9), 158 (11), 156 (base peak), and 87 (18). Anal. Calcd for $C_9H_{21}NSSi$: C, 53.14; H, 10.41; N, 6.89. Found: C, 53.22; H, 10.30; N, 6.79.

3 (mixture of *E* and *Z* isomers (*E*:*Z* = 3:2)): colorless liquid; bp 120 °C (0.3 mmHg); IR (neat) 1620, 1245, and 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.04 (9 H, s, Me_3Si), 1.12 (1.2 H, t, Me of Et), 1.15 (1.8 H, t, Me of Et), 2.20 (1.2 H, s, SMe), 2.2–2.6 (2 H, m, CH_2 of Et), 2.38 (1.8 H, s, SMe), 3.18 (1.2 H, s, CH_2SiMe_3), and 3.27 (0.8 H, s, CH_2SiMe_3); MS, *m/z* (relative intensity) 189 (M^+, 32), 174 (23), 159 (23), 158 (37), 144 (40), 142 (70), 119 (18), 87 (44), 73 (98), 69 (60), and 59 (base peak). Anal. Calcd for $C_8H_{19}NSSi$: C, 50.73; H, 10.11; N, 7.39. Found: C, 50.60; H, 10.41; N, 7.21.

α-(Benzoylthio)-*N*-[(trimethylsilyl)methyl]benzylideneamine (4). A mixture of *N*-[(trimethylsilyl)methyl]thiobenzamide

(27) Turro, N. J.; Cha, Y.; Gould, I. R.; Padwa, A.; Gasdaska, J.; R.; Tomas, M. *J. Org. Chem.* **1985**, *50*, 4415.

(0.22 g, 1 mmol), benzoyl chloride (0.12 mL, 1 mmol), and triethylamine (0.14 mL, 1 mmol) in dry benzene (3 mL) was stirred at room temperature for 6 h. The mixture was treated with diethyl ether (10 mL), washed with water (10 mL × 2), dried over magnesium sulfate, and then evaporated in vacuo. The residue was chromatographed over silica gel with hexane–ethyl acetate (2:1) to give **4** (0.3 g, 92%): orange prisms (benzene–hexane); mp 43–45 °C; IR (KBr) 1680, 1250, and 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (9 H, s, Me_3Si), 4.19 (2 H, s, CH_2), and 6.8–7.4 (10 H, m, Ph); MS, m/z (relative intensity) 327 (M^+, 17), 312 (28), 222 (47), 209 (27), 121 (base peak), 117 (35), 105 (77), 91 (33), and 77 (82). Anal. Calcd for $C_{18}H_{21}NOSSi$: C, 66.01; H, 6.46; N, 4.28. Found: C, 66.09; H, 6.39; N, 4.21.

***N*-[(Trimethylsilyl)methyl] Bis(methylthio) Imine (5).** [(Trimethylsilyl)methyl]amine (1.03 g, 10 mmol) was added dropwise to carbon disulfide (10 mL) at 0 °C under nitrogen. After a few minutes, methyl iodide (1.42 g, 10 mmol) was added dropwise at 0 °C. The mixture was stirred at room temperature for 8.5 h, poured into ice water, and extracted with diethyl ether (30 mL × 2). The combined extracts were dried over magnesium sulfate and then evaporated in vacuo. The residue was distilled on a Kugelrohr apparatus to give **5** (1.9 g, 92%): colorless liquid; bp 80 °C (0.8 mmHg) (bulb to bulb); IR (neat) 1580, 1420, 1245, and 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.09 (9 H, s, Me_3Si), 2.30, 2.46 (each 3 H, s, SMe), and 3.30 (2 H, s, CH_2); MS, m/z (relative intensity) 207 (M^+, 8), 160 (17), 102 (19), 91 (39), 87 (68), 73 (base peak), 72 (43), 61 (33), and 59 (48). Calcd for $C_7H_{17}NS_2Si$: C, 40.53; H, 8.26; N, 6.75. Anal. Found: C, 40.79; H, 8.30; N, 6.70.

General Procedure for the Water-Induced Cycloadditions of *N*-(Silylmethyl) Thioimidates with Olefins Leading to 6–8. To the mixture of an *N*-(silylmethyl) thioimidate and an olefin (each 1 mmol) in HMPA (3 mL) was added water (18 mg, 1 mmol) or water–acetic acid (each 1 mmol). After the mixture was allowed to react under the reaction conditions listed in Table I, it was poured into water (30 mL) and extracted with diethyl ether (30 mL × 2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel with hexane–ethyl acetate (10:1 to 1:1) to give thiol-eliminated cycloadducts **6–8**. The results are shown in Table I.

General Procedure for the Trifluoromethanesulfonic Acid Induced Cycloadditions of *N*-(Silylmethyl) Thioimidates with Olefins. The mixture of an *N*-(silylmethyl) thioimidate and trifluoromethanesulfonic acid (each 1 mmol) in dry 1,2-dimethoxyethane (DME) was stirred under nitrogen at room temperature for 1 h. An olefin and then cesium fluoride (each 1 mmol) were added. The mixture was stirred under nitrogen at room temperature for 13 h, diluted with chloroform (30 mL), and then washed with water (50 mL × 2). The organic layer separated was dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel with hexane–ethyl acetate. The results are listed in Table I.

Compounds **6a**, **6c**, **7a**, **7d**, **8a**, and **8b** are all known, and their structures were confirmed by the comparison of spectral data.[9]

6b: colorless liquid; IR (neat) 1770, 1700, and 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (6 H, d, Me of *i*-Pr), 2.80 (1 H, m, CH of *i*-Pr), 3.58 (1 H, m, 6a-H), and 4.1–4.5 (3 H, m, 3a- and 6-H); MS, m/z (relative intensity) 194 (M^+, 50), 179 (base peak), 113 (20), 83 (90), and 68 (31). Anal. Calcd for $C_{10}H_{14}N_2O_2$: C, 61.83; H, 7.26; N, 14.42. Found: C, 61.80; H, 7.12; N, 14.50.

7b: colorless liquid; IR (neat) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08 (6 H, d, Me of *i*-Pr), 2.80 (1 H, m, CH of *i*-Pr), 3.3-3.8 (1 H, m, 4-H), 3.62, 3.68 (each 3 H, s, COOMe), and 4.4–4.7 (3 H, m, 3- and 5-H); MS, m/z 227 (M^+) and 179 (base peak). Anal. Calcd for $C_{11}H_{17}NO_4$: C, 58.14; H, 7.54; N, 6.16. Found: C, 58.20; H, 7.41; N, 6.05.

7c: colorless prisms (benzene–hexane); mp 68.5–70 °C; IR (KBr) 1725, 1715, and 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29, 1.45 (each 9 H, s, *t*-Bu), 3.46 (1 H, ddd, J = 7.3, 5.0, and 5.0 Hz, 4-H), 4.2-4.5 (3 H, m, 3- and 5-H), 7.3–7.4 (3 H, m, Ph), and 7.7–7.9 (2 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 27.71, 28.06 (each q, *t*-Bu), 48.29 (d, 4-C), 58.30 (d, 3-C), 64.59 (t, 5-C), 81.65, 82.06 (each s, *q*-C), 128.41, 130.83 (each d), 133.42 (s), 169.42, 170.13 (each s, COO-Bu-*t*), and 172.41 (s, 2-C); MS, m/z (relative intensity) 346 (M^+ + 1, 70), 289 (21), 233 (68), 216 (31), 188 (51), 187 (21), 144 (33), 117 (20), and 57 (base peak). Anal. Calcd for $C_{18}H_{27}NO_4$: C, 69.54; H, 7.87; N, 4.06. Found: C, 69.28; H, 7.82; N, 4.32.

8c: colorless liquid; IR (neat) 1725, 1640, and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (3 H, dd, J = 9.0 and 1.0 Hz, 4-Me), 3.12 (1 H, m, 4-H), 3.62 (1 H, s, 3-H), 3.69 (3 H, s, COOMe), 3.71 (1 H, m, 4-H), 4.10 (1 H, dd, J = 7.5 and 1.0 Hz, one of 5-H), 4.27 (1 H, d, J = 8.2 Hz, the other of 5-H), 7.2–7.5 (3 H, m, Ph), and 7.6–7.9 (2 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 11.41 (q, 4-Me), 47.36 (d, 4-C), 53.12 (d and q, 3-C and COOMe), 64.00 (t, 5-C), 127.83, 128.65 (each d), 132.60 (s), 172.01, and 173.66 (each s, COOMe and 2-C); MS, m/z 217 (M^+) and 117 (base peak). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.95; N, 6.44. Found: C, 71.80; H, 6.74; N, 6.39.

8d: colorless prisms (benzene–hexane); mp 159 °C; IR (KBr) 1725 and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.48 (3 H, s, COOMe), 3.94 (1 H, dd, J = 9.0 and 8.3 Hz, 4-H), 4.12 (1 H, s, 3-H), 4.42 (1 H, d, J = 8.3 Hz, one of 5-H), 4.45 (1 H, d, J = 9.0 Hz, the other of 5-H), 7.2–7.4 (8 H, m, Ph), and 7.7–7.9 (2 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 49.23 (d, 3-C), 52.41 (q, COOMe), 62.41 (d, 4-C), 68.94 (t, 5-C), 126.70, 127.18, 128.18, 128.59, 128.71, 129.06 (each d), 130.41, 134.48 (each s), 168.71 (s, COOMe), and 172.06 (s, 2-C); MS, m/z (relative intensity) 279 (M^+, 2), 133 (22), 131 (28), 118 (23), 117 (base peak), 116 (29), 105 (42), 104 (91), 103 (59), 91 (38), 90 (24), 89 (24), 78 (28), and 77 (86). Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.39; H, 6.13; N, 5.01. Found: C, 77.28; H, 6.01; N, 5.25.

8e: colorless liquid; IR (neat) 1725, 1655, and 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.52 (3 H, s, 3-Me), 2.03 (1 H, ddd, J = 12.6, 7.5, and 5.8 Hz, one of 4-H (cis to 3-Me)), 2.55 (1 H, ddd, J = 12.6, 8.7, and 7.0 Hz, the other of 4-H (trans to 3-Me)), 3.67 (3 H, s, COOMe), 4.1-4.2 (2 H, m, 5-H), and 7.3–7.8 (5 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 21.28 (q, 3-Me), 39.79 (t, 4-C), 52.53 (q, COOMe), 58.49 (s, 3-C), 58.88 (t, 5-C), 127.83, 128.71, 130.41 (each d), 133.10 (s), 173.28 (s, 2-C), and 175.92 (s, COOMe); MS, m/z (relative intensity) 217 (M^+, 6), 158 (24), 156 (17), 117 (base peak), 116 (29), 115 (50), 104 (25), 103 (21), 91 (24), 89 (25), and 77 (76). Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.77; H, 6.93; N, 6.25.

General Procedure for the Fluoride-Induced Additions of *N*-(Silylmethyl) Thioimidates and *N*-(Silylmethyl) Bis(methylthio) Imine with Dimethyl Fumarate or Maleate Leading to 9. Tetrabutylammonium fluoride (TBAF, 1 M solution in THF, 0.1 equiv) was added to the solution of an equimolar mixture of an *N*-(silylmethyl) thioimidate (or bis(methylthio) imine) and dimethyl fumarate (or maleate) in dry THF (2 mL for 1 mmol of the reagents) at 0 °C under nitrogen. The mixture was allowed to react under the conditions listed in Table II, poured into ice water, and extracted with diethyl ether (30 mL × 2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. Pure **9a**, **9b**, or **9c** was obtained through micro vacuum distillation of the residue, while pure **9c** was afforded through column chromatography over silica gel using a mixture of hexane–ethyl acetate (2:1). The results are given in Table II.

9a (mixture of *E* and *Z* isomers (*E*:*Z* = 3:2)): pale yellow liquid; bp 205 °C (0.3 mmHg) (bulb to bulb); IR (neat) 1738 and 1618 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.09 (1.2 H, s, SMe), 2.32 (1.8 H, s, SMe), 2.4–2.9 (2 H, m, CH_2COOMe), 3.0–3.4 (1 H, m, CHCOOMe), 3.5–3.9 (2 H, m, NCH_2), 3.62, 3.63, 3.65, 3.71 (6 H, each s, COOMe), and 7.1–7.4 (5 H, m, Ph); MS, m/z (relative intensity) 309 (M^+, 3), 262 (64), 159 (base peak), 127 (57), 105 (21), 99 (21), 91 (28), and 59 (35). Anal. Calcd for $C_{15}H_{19}NO_4S$: C, 58.23; H, 6.19; N, 4.53. Found: C, 58.17; H, 6.22; N, 4.54.

9b (mixture of *E* and *Z* isomers (*E*:*Z* = 1:1)): colorless liquid; bp 170 °C (6 mmHg); IR (neat) 1730 and 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11, 1.13 (each 3 H, d, Me of *i*-Pr), 2.12, 2.40 (each 1.5 H, s, SMe), 2.5–2.9 (2 H, m, CH_2COOMe), 2.9–3.3 (2 H, m, CH of *i*-Pr and CHCOOMe), 3.4–3.8 (2 H, m, NCH_2), 3.64, 3.66, and 3.77 (6 H, each s, COOMe); MS, m/z (relative intensity) 275 (M^+, 3), 228 (32), 159 (90), 127 (50), 99 (18), 69 (25), and 43 (base peak). Anal. Calcd for $C_{12}H_{21}NO_4S$: C, 52.33; H, 7.68; N, 5.14. Found: C, 52.30; H, 7.77; N, 5.20.

9c (mixture of *E* and *Z* isomers (*E*:*Z* = 1:1)): colorless liquid; IR (neat) 1740 and 1627 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–1.4 (3 H, Me of Et), 2.20, 2.40 (each 1.5 H, s, SMe), 2.3–2.9 (2 H, m, CH_2COOMe), 3.4–3.8 (5 H, m, CHCOOMe, NCH_2, and CH_2 of Et), 3.60, and 3.65 (each 3 H, s, COOMe); MS, m/z 261 (M^+) and 159 (base peak). Anal. Calcd for $C_{11}H_{19}NO_4S$: C, 50.55; H, 7.32;

N, 5.35. Found: C, 50.45; H, 7.30; N, 5.19.

9d: pale yellow liquid; bp 100 °C (0.6 mmHg) (bulb to bulb); IR (neat) 1730 and 1579 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.25, 2.46 (each 3 H, s, SMe), 2.5–3.0 (2 H, m, CH_2COOMe), 3.0–3.8 (3 H, m, CHCOOMe and NCH_2), 3.59, and 3.60 (each 3 H, s, COOMe); MS, m/z (relative intensity) 279 (M^+, 37), 248 (17), 232 (29), 159 (base peak), 127 (65), 99 (27), and 74 (25). Anal. Calcd for $C_{10}H_{17}NO_4S_2$: C, 42.99; H, 6.13; N, 5.01. Found: C, 42.80; H, 6.12; N, 5.12.

General Procedure for the Fluoride-Induced Cycloadditions of *N*-(Silylmethyl) Thioimidates and *N*-(Silylmethyl) Bis(methylthio) Imine with 3-Penten-2-one, Methyl Acrylate, Acrylonitrile, or Methyl Methacrylate Leading to 10 and 11. The equimolar mixture of an *N*-(silylmethyl) thioimidate (or bis(methylthio) imine) and an olefin was treated with 10 mol % of TBAF under the conditions listed in Tables II and III. After the reaction was completed, the mixture was poured into ice water and extracted with diethyl ether (25 mL × 2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was then chromatographed over silica gel using a mixture of hexane–ethyl acetate (2:1 to 4:1) to give **10** or **11**. The results are shown in Tables II and III.

10a: colorless liquid; IR (neat) 1710 and 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.20 (3 H, s, COMe), 2.9–3.6 (3 H, m, 3- and 4-H), 3.9–4.5 (2 H, m, 5-H), 7.2–7.5 (3 H, m, Ph), and 7.5–7.9 (2 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 28.94 (q, COMe), 37.00 (t, 3-C), 49.83 (d, 4-C), 63.82 (t, 5-C), 127.89, 128.72, 130.95 (each d), 134.01 (s), 172.41 (s, 2-C), and 210.54 (s, COMe); MS, m/z (relative intensity) 187 (M^+, 23), 144 (base peak), 143 (19), 117 (37), and 77 (21). Anal. Calcd for $C_{12}H_{13}NO$: C, 76.97; H, 6.99; N, 7.48. Found: C, 76.81; H, 7.10; N, 7.54.

10b: colorless liquid; IR (neat) 1710 and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1–1.4 (6 H, m, Me of *i*-Pr), 2.25 (3 H, s, COMe), 2.4–2.9 (1 H, m, CH of *i*-Pr), 3.1–3.6 (3 H, m, 3- and 4-H), and 3.7–4.1 (2 H, m, 5-H); MS, m/z 153 (M^+) and 117 (base peak). Anal. Calcd for $C_9H_{15}NO$: C, 70.54; H, 9.86; N, 9.14. Found: C, 70.38; H, 9.82; N, 9.10.

10c: colorless liquid: IR (neat) 1710 and 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–1.4 (3 H, m, Me of Et), 2.25 (3 H, s, COMe), 3.1–3.6 (5 H, CH_2 of Et and 3- and 4-H), and 3.6–4.1 (2 H, m, 5-H); MS, m/z 139 (M^+) and 117 (base peak). Anal. Calcd for $C_8H_{13}NO$: C, 69.03; H, 9.41; N, 10.06. Found: C, 69.21; H, 9.55; N, 9.95.

10d: colorless liquid; IR (neat) 1710 and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.20 (3 H, s, COMe), 2.25 (3 H, s, SMe), 3.0–3.5 (3 H, m, 3- and 4-H), and 3.6-4.1 (2 H, m, 5-H); MS, m/z 157 (M^+) and 128 (base peak). Anal. Calcd for $C_7H_{11}NOS$: C, 53.47; H, 7.05; N, 8.91. Found: C, 53.61; H, 7.11; N, 8.81.

10e: pale yellow liquid; IR (neat) 1720 and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.2–3.4 (3 H, m, 3- and 4-H), 3.70 (3 H, s, COOMe), 4.2–4.4 (2 H, m, 5-H), 7.2–7.5 (3 H, m, Ph), and 7.7–7.9 (2 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 38.76 (t, 3-C), 41.59 (d, 4-C), 52.24 (q, COOMe), 64.89 (t, 5-C), 127.89, 128.72, 130.95 (each d), 134.01 (s), 172.07 (2-C), and 175.13 (s, COOMe); MS, m/z (relative intensity) 203 (M^+, 4), 144 (20), 117 (52), 116 (22), 115 (52), 103 (48), 91 (30), 90 (20), 89 (30), 78 (58), 77 (23), 63 (27), and 59 (base peak). Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.91; H, 6.44; N, 6.89. Found: C, 71.17; H, 6.40; N, 6.79.

10f: colorless liquid; IR (neat) 1720 and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1–1.3 (6 H, m, Me of *i*-Pr), 2.5–2.9 (1 H, m, CH of *i*-Pr), 3.0–3.5 (3 H, m, 3- and 4-H), 3.6–4.1 (2 H, m, 5-H), and 3.64 (3 H, s, COOMe); MS, m/z 169 (M^+) and 117 (base peak). Anal. Calcd for $C_9H_{15}NO_2$: C, 63.87; H, 8.93; N, 8.27. Found: C, 63.77; H, 8.67; N, 8.27.

10g: pale yellow liquid; IR (neat) 2240 and 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.1–3.4 (3 H, m, 3- and 4-H), 4.3–4.5 (2 H, m, 5-H), 7.2–7.6 (3 H, m, Ph), and 7.6–7.9 (2 H, m, Ph); MS, m/z (relative intensity) 170 (M^+, 20), 117 (base peak), 77 (22), and 61 (28). Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.61; H, 5.92; N, 16.46. Found: C, 77.50; H, 6.08; N, 16.30.

11a: pale yellow liquid; IR (neat) 1725 and 1618 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (3 H, s, 4-Me), 2.86 (1 H, ddd, J = 17.3, 2.2, and 1.0 Hz, one of 3-H), 3.57 (1 H, dt, J = 17.3, 2.0, and 2.0 Hz, the other of 3-H), 3.69 (3 H, s, COOMe), 3.93 (1 H, ddd, J = 16.4, 2.0, and 1.0 Hz, one of 5-H), 4.37 (1 H, ddd, J = 16.4, 2.2, and 2.0 Hz, the other of 5-H), 7.4–7.5 (3 H, m, Ph), and 7.7–7.9 (2 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 24.76 (q, 4-Me), 47.00 (t, 3-C), 48.35 (s, 4-C), 52.35 (q, COOMe), 72.18 (t, 5-C), 127.77, 128.72, 130.89 (each d), 134.25 (s), 171.60 (s, 2-C), and 177.19 (s, COOMe); MS, m/z (relative intensity) 217 (M^+, 25), 158 (71), 117 (base peak), and 77 (24). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.80; H, 7.10; N, 6.31.

11b: colorless liquid; IR (neat) 1720 and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0–1.2 (6 H, m, Me of *i*-Pr), 1.50 (3 H, s, 4-Me), 2.6–3.0 (2 H, m, CH of *i*-Pr and one of 3-H), 3.5–3.7 (1 H, m, the other of 3-H), 3.60 (3 H, s, COOMe), 3.8–4.1 (1 H, m, one of 5-H), and 4.1–4.3 (1 H, m, the other of 5-H); MS, m/z 183 (M^+) and 41 (base peak). Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.53; H, 9.35; N, 7.64. Found: C, 65.41; H, 9.25; N, 7.62.

11c: colorless liquid; IR (neat) 1710 and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (3 H, s, 4-Me), 2.24 (3 H, s, SMe), 3.1–3.8 (2 H, m, 3-H), 3.50 (3 H, s, COOMe), and 4.0–4.4 (2 H, m, 5-H); MS, m/z 187 (M^+) and 128 (base peak). Anal. Calcd for $C_8H_{13}NO_2S$: C, 51.13; H, 6.99; N, 7.48. Found: C, 51.02; H, 6.98; N, 7.45.

Reaction of *N*-(Silylmethyl) Thioimidate 1 with Methyl Crotonate in the Presence of TBAF Leading to 12a + 13a. To a mixture of **1** (118 mg, 0.5 mmol) and methyl crotonate (75 mg, 0.75 mmol) in dry THF (1.5 mL) was added TBAF (1 M solution, 0.05 mL, 0.05 mmol) at 0 °C under nitrogen. After 0.5 h, the mixture was warmed to room temperature and stirred for 4 h. The mixture was poured into ice water and extracted with diethyl ether (30 mL × 2). The combined extracts were dried and evaporated in vacuo. The residue was subjected to GLC analysis at this stage (**12a:13a** = 24:76) and then chromatographed over silica gel with hexane–ethyl acetate (2:1) to give **12a** (16 mg, 15%) and then **13a** (63 mg, 48%).

12a: pale yellow liquid; IR (neat) 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (3 H, d, 3-Me), 3.6–3.9 (1 H, m, 4-H), 3.70 (3 H, s, COOMe), 4.1–4.4 (3 H, m, 3- and 5-H), 7.2–7.5 (3 H, m, Ph), and 7.6–7.8 (2 H, m, Ph); MS, m/z 217 (M^+) and 117 (base peak). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.95; N, 6.44. Found: C, 71.82; H, 6.87; N, 6.51.

13a (mixture of two diastereomers): pale yellow liquid; IR (neat) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2–1.3 (3 H, m, Me), 2.05, 2.35 (3 H, each s, SMe), 2.2–2.7 (2 H, m, CH_2COOMe), 3.4–3.8 (3 H, CH and CH_2N), 3.59 (3 H, s, COOMe), and 7.1–7.5 (5 H, m, Ph); MS, m/z 265 (M^+) and 115 (base peak). Anal. Calcd for $C_{14}H_{19}NO_2S$: C, 63.33; H, 7.21; N, 5.27. Found: C, 63.40; H, 7.21; N, 5.40.

Reaction of *N*-(Silylmethyl) Thioimidate 1 with Methyl Cinnamate in the Presence of TBAF Leading to 12b + 13b. A similar reaction of **1** (118 mg, 0.5 mmol) with methyl cinnamate (126 mg, 0.75 mmol) in dry THF (2 mL) was carried out under nitrogen in the presence of TBAF (0.05 mL, 0.05 mmol). The reaction conditions are shown in Table II. GLC analysis of the crude reaction mixture indicated the formation of **12b** and **13b** (**12b:13b** = 19:81). The mixture was chromatographed over silica gel using hexane–ethyl acetate (2:1) to give **12b** (20 mg, 14%) and then **13b** (99 mg, 61%).

12b: pale yellow liquid; IR (neat) 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.5–3.9 (1 H, m, 4-H), 3.60 (3 H, s, COOMe), 4.0–4.6 (3 H, m, 3- and 5-H), 6.9–7.4 (8 H, m, Ph), and 7.6–7.9 (2 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 49.35 (d, 4-C), 52.59 (q, COOMe), 62.59 (d, 3-C), 69.12 (d, 5-C), 126.83, 127.30, 128.12, 128.83, 129.18 (each d), 131.06, 143.65 (each s), 168.83 (s, 2-C), and 172.24 (s, COOMe); MS, m/z (relative intensity) 279 (M^+, 16), 220 (15), 176 (10), 118 (11), and 117 (base peak). Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.39; H, 6.13; N, 5.01. Found: C, 77.30; H, 6.24; N, 5.11.

13b (mixture of two diastereomers): colorless liquid; IR (neat) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.00, 2.34 (3 H, each s, SMe), 2.5–3.1 (2 H, m, CH_2COOMe), 3.4–3.9 (3 H, m, CH and CH_2N), 3.50 (3 H, s, COOMe), and 6.9–7.4 (10 H, m, Ph); MS, m/z (relative intensity) 327 (M^+, 8), 280 (59), 177 (66), 135 (23), 117 (base peak), 91 (20), and 77 (21). Anal. Calcd for $C_{19}H_{21}NO_2S$: C, 69.69; H, 6.46; N, 4.27. Found: C, 69.60; H, 6.60; N, 4.46.

General Procedure for the Fluoride-Induced Cycloadditions of *N*-(Silylmethyl) Thioimidates with Carbonyl Compounds Leading to 14 and 15. To the solution of an *N*-(silylmethyl) thioimidate (1 mmol) and a carbonyl compound (2 mmol) in dry THF (2–4 mL) was added TBAF (0.05 mL, 0.05 mmol) at room temperature. The mixture was allowed to react under the conditions listed in Table IV, poured into ice water, and then extracted with diethyl ether (30 mL × 2). The combined

extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel with hexane–ethyl acetate (2:1) to give a cycloadduct **14** or **15**. As compounds **14a**, **14c**, and **14d** were previously prepared in our laboratory, their structures were determined by the comparison of spectral data.[9]

14b: colorless liquid; IR (neat) 1655 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16 (6 H, d, Me of *i*-Pr), 3.0–3.3 (1 H, m, CH of *i*-Pr), 3.70 (1 H, dd, J = 12.0 and 8.0 Hz, one of 4-H), 4.12 (1 H, dd, J = 12.0 and 9.0 Hz, the other of 4-H), 5.45 (1 H, dd, J = 9.0 and 8.0 Hz, 5-H), and 7.1–7.5 (5 H, m, Ph); MS, m/z 189 (M^+) and 77 (base peak). Anal. Calcd for $C_{12}H_{15}NO$: C, 76.15; H, 7.98; N, 7.40. Found: C, 76.07; H, 7.92; N, 7.27.

15a: colorless liquid; IR (neat) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.68 (2 H, s, 4-H), 7.1–7.7 (8 H, m, Ph), 7.7–7.9 (5 H, m, Ph), and 8.0–8.2 (2 H, m, Ph); MS, m/z (relative intensity) 182 (M^+ – 117, 41), 105 (base peak), and 77 (71). Anal. Calcd for $C_{21}H_{17}NO$: C, 84.42; H, 5.72; N, 4.67. Found: C, 84.31; H, 5.60; N, 4.70.

15b: colorless liquid; IR (neat) 1642 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.77 (3 H, s, Me), 4.07 (2 H, s, 4-H), 7.0–7.5 (8 H, m, Ph), and 7.7–8.0 (2 H, m, Ph); MS, m/z (relative intensity) 237 (M^+, 9), 118 (11), 117 (base peak), 105 (10), and 76 (27). Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.87; H, 6.42; N, 5.63.

Chemistry of Azido Quinones. Cyanophenols from 4-Alkynyl-3-azido-1,2-benzoquinones

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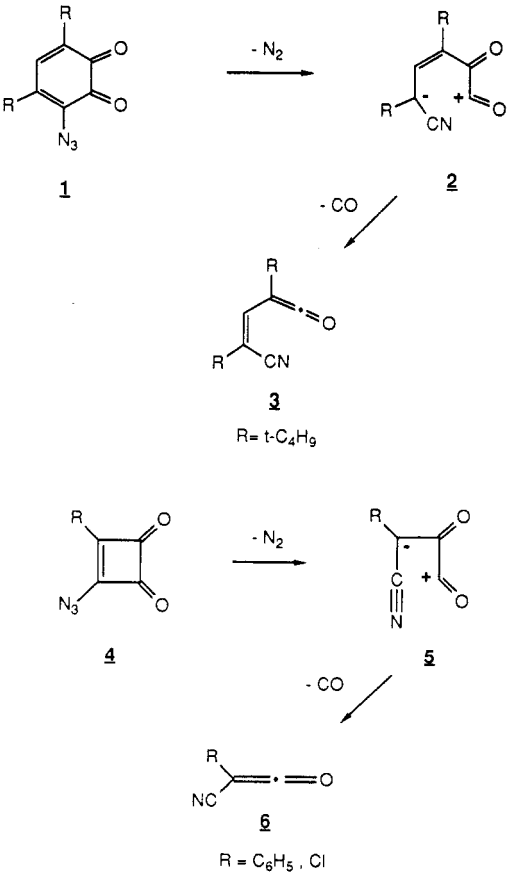
4-Alkynyl-3-azido-6-chloro-5-ethoxy-1,2-benzoquinones are shown to undergo thermolysis to (2-alkynyl-2-cyanoethenyl)ketenes. These conjugated ketenes undergo intramolecular cyclization to zwitterionic intermediates that proceed to highly subsituted 4-cyanophenols via inter- or intramolecular trapping by nucleophilic attack at the aryl cation site. The mechanism and scope of these unusual transformations are discussed.

The thermal chemistry of azido-1,4-benzoquinones has received detailed study. These compounds have been shown to function as precursors to a large variety of carbocyclic, heterocyclic, and acyclic systems.[1,2] In this context, the most useful reaction is their conversion to cyanoketenes.[3] Azido-1,2-benzoquinones, unlike the 1,4-regioisomers, have received very little attention, but here also their conversion to cyanoketenes has recently been reported. For example, 3-azido-1,2-benzoquinones have been shown to give vinylketenes upon thermolysis in refluxing benzene.[4] A specific example is the conversion of 3-azido-4,6-di-*tert*-butyl-1,2-benzoquinone (**1**) to the zwitterion **2**, which gives the remarkably stable vinylketene **3** upon loss of carbon monoxide (Scheme I). In a related series, azidocyclobutenediones **4** fragment even at low temperature (–30 °C) to carbon monoxide, dinitrogen, and the corresponding cyanoketene **6**; the zwitterionic intermediate **5** has been proposed as the ultimate intermediate (Scheme I).[5-8]

Reported in this manuscript are the details of a study of the in situ thermolytic conversion of 4-alkynyl-3-azido-1,2-benzoquinones **7** to (2-alkynyl-2-cyanoethenyl)-ketenes **8**. Conjugated ketenes of this type have not previously been reported.[9] They express unusual chemistry in undergoing cyclization to the proposed zwitterions **9** and these proceed to cyanophenols **10** upon inter- or intramolecular trapping by nucleophiles (Nu). This transformation is generally outlined in Scheme II. For the study reported here, the azidoquinones investigated are all 4-alkynyl-3-azido-6-chloro-5-ethoxy-1,2-benzoquinones. These are available from the corresponding dichloro-

Scheme I



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