Diels-Alder Reactions of 2-[(Trialkylsilyl)oxy]pyrylium Cations of 2*H*-Pyran-2-one and 2*H*-1-Benzopyran-2-one Derivatives

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The reactions of 6-methyl-2*H*-pyran-2-one and 2*H*-1-benzopyran-2-one with the 2-(trialkylsilyl)oxy dienes **6a-d** in the presence of *tert*-butyldimethylsilyl triflate gave the [4 + 2] cycloadducts **7a-c** and **8a-d** regio- and stereoselectively in moderate yields. The ring junction in the cycloadducts is cis. The stereochemistry of **8a-d** is discussed in terms of the ^{1}H NMR spectra of the compounds. Similar reactions of 3-(ethoxycarbonyl)-2-pyrones and 3-(alkoxycarbonyl)coumarins with the 2-(trialkylsilyl)oxy dienes **6a-e** gave the cycloadducts **14-18** in satisfactory yields. Dehydrogenation of **7c**, **8b**, and **8c** with DDQ in refluxing toluene afforded **23-25**, respectively.

Introduction

The ability of 2*H*-pyran-2-ones (α-pyrones) to undergo Diels-Alder reactions with electron-deficient dienophiles to yield dienes and arenes is widely recognized.[1] Boger and Mullican[2] described the inverse electron-demand Diels-Alder reactions of electron-rich dienophiles (Scheme I, top). Therein, 3-carbomethoxy-2-pyrones served as electron-deficient dienes.[2] Sammes[3a] reported the cycloaddition of 3-oxidopyrylium systems to various olefins. Wender et al.[3b,c] developed a method for the synthesis of phorbol that featured such a cycloaddition. In an earlier paper,[4a] we reported stereoselective cyclohexene annulations by the reaction of 4-[(*tert*-butyldimethylsilyl)oxy]-1-benzopyrylium salts with α,β-unsaturated ketones. We now describe the Diels-Alder reactions of α-pyrone and coumarin derivatives with 2-(trialkylsilyl)oxy dienes. Herein the α-pyrones act as electron-deficient dienophiles (Scheme I, bottom).[4b,4c]

Many heterocycles possess interesting pharmacological properties. Among these, modified oxasteroids have attracted a great deal of attention from synthetic organic chemists.[5] Some of the cycloadducts obtained by the reactions described here are potential precursors of oxasteroids[6] or aglycons.[7]

Scheme I

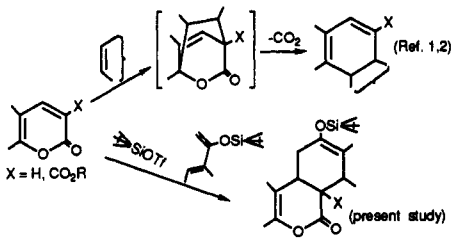
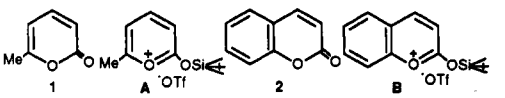


Table I. ^{1}H NMR Chemical Shifts of Ring Protons in 1, 2 and A, B



compd	chemical shift (δ, ppm) H_3	H_4	H_5
1	5.90	7.15	6.07
A	6.59	7.91	6.69
2	6.50	7.91	
B	6.81	8.42	

Results and Discussion

Reactions of 2-[(Trialkylsilyl)oxy]pyrylium Salts. The 2-[(trialkylsilyl)oxy]pyrylium salt A was easily prepared by treating neat 6-methyl-2*H*-pyran-2-one (1) with *tert*-butyldimethylsilyl triflate for 1 h at 0 °C. Although an α,β-unsaturated carbonyl moiety exists in coumarin (2), the corresponding 2-[(trialkylsilyl)oxy]benzopyrylium salt B was not formed under the same conditions (80 °C, 1 h, neat) that were used for the preparation of 4-[(trialkylsilyl)oxy]benzopyrylium cations.[4c] The formation of 2-(trialkylsiloxy)benzopyrylium salt B required heating coumarin neat with *tert*-butyldimethylsilyl triflate at 160 °C for 16 h.

That A and B were formed was confirmed by ^{1}H NMR spectroscopy. In the spectra of $CHCl_3$ solutions of A and B, the signals due to H_3 and H_4 were shifted downfield by 0.3-0.7 ppm relative to the signals due to the corresponding protons of 1 and 2 (Table I). The signals of A and B did not change at all upon dilution and they showed the same chemical shifts even when a half equivalent of the silyl triflate was used relative to 1 or 2 (1:1 mixture of 1 and A, or that of 2 and B).

Treatment of CH_2Cl_2 solutions of the salts A and B with the ketene silyl acetal 3 at room temperature in the presence of 2,6-lutidine afforded the 4-substituted 3,4-dihydro-α-pyrone derivatives 4 and 5 in yields of 40 and 80%, respectively (eq 1). However, under the same conditions, treatment of A with the 2-(trialkylsilyl)oxy dienes

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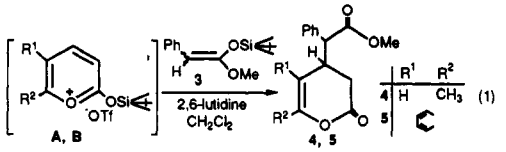
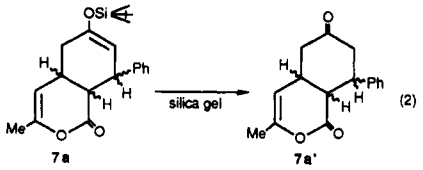


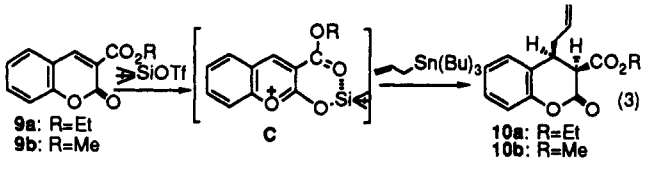
6a–c gave the cycloadducts 7a–c in very poor yield. The reaction of salt B with 2-silyloxy diene 6a under the same conditions gave cycloadduct 8a in 35% yield.

The same products were obtained by treating a THF solution of 1 or 2 with, successively, 1 equiv of *tert*-butyldimethylsilyl triflate and a THF solution of each of the 2-(trialkylsilyl)oxy dienes 6a–c and 2,6-lutidine. The reaction of 2 with 6d afforded 8d in moderate yield under these conditions, whereas treatment of 1 with 6d did not give the desired cycloadduct. The structures assigned to 7a–c and 8a–d are based upon the ^{1}H NMR spectra and chemical behavior of the compounds. One of the cycloadducts 7a was readily desilylated by exposure to atmospheric moisture or to silica gel to give the corresponding ketone 7a′ (eq 2). The results obtained by this second



method are summarized in Table II. The method gave better yields than the method that used CH_2Cl_2 solutions of pregenerated A and B and also obviated the high temperature (160 °C, 16 h) required for the preparation of B.

To activate the α-pyrone ring toward reaction with the 2-(trialkylsilyl)oxy dienes, an alkoxycarbonyl group was introduced into the 3-position. The activated 3-(alkoxycarbonyl)coumarins 9a,b were prepared by known procedures.[8] The α-pyrones 11–13 were synthesized by Boger's methods.[2d] The activated 2-(trialkylsiloxy)pyrylium salts C were formed readily (within 30 min) by the reaction of 9a,b and *tert*-butyldimethylsilyl triflate in CH_2Cl_2 solution at room temperature. The salts showed greater reactivity than B. In fact, the reaction of salts C with allyltributylstannane proceeded smoothly to afford the 4-allyl-3,4-dihydrocoumarin derivatives 10a,b in yields of 45 and 60%, respectively (eq 3). On the other hand, under the



same conditions, B did not react with this allylation reagent. The relative ease of formation of salts C and their greater reactivity can be ascribed to the electron-withdrawing effect of the alkoxycarbonyl group of 9a,b and the additional stabilization of the salt C provided by the intramolecular coordination of the trialkylsilyl group with the carbonyl group.

The ^{1}H NMR spectra of both 10a and 10b show a small H_3–H_4 coupling constant (J = 2.9–3.1 Hz). This indicates that the two hydrogens are cis to each other and that the alkoxycarbonyl group is in an equatorial position and the allyl group is in an axial position (vide infra).

The reaction of the activated α-pyrones 9 and 11–13 with the 2-(trialkylsilyl)oxy dienes 6a–e in the presence of

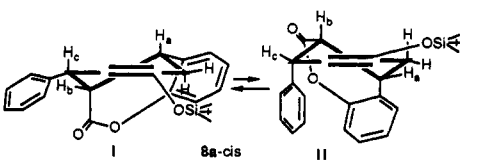


Figure 1.

tert-butyldimethylsilyl triflate easily afforded 14–18 in the moderate yield. These yields were better than those obtained from α-pyrones 1 and 2 (Table II). The products 14–18 were readily purified without desilylation by column chromatography on silica gel. The results are summarized in Table III.

Stereochemical and Mechanistic Considerations. The stereochemistry of the ring junction of 7a–c was not established because the signals characteristic of the protons at the ring junction could not be identified in the respective ^{1}H NMR spectra. The structures of 8a–d were tentatively established from the ^{1}H NMR spectra of the compounds. Additional evidence in support of the assigned structures came from the ^{1}H NMR spectra of the ketones 19a–c, which were obtained by desilylation of 8a–c. The signals characteristic of 8a–d and derivatives are summarized in Table IV.

In the ^{1}H NMR spectrum of 8d-*cis*, a doublet (J = 0.4 Hz) due to the vinyl proton (R^5) appears at δ 4.70. Signals due to H_a and H_b are seen at δ 3.46 (dt, J = 4.8 and 9.4 Hz) and δ 2.70 (d, J = 4.8 Hz), respectively. In the case of 8a-*cis*, the signal due to the vinyl proton (R^5) appears at δ 5.20 as a doublet of triplets (J = 3.0 and 1.5 Hz). Signals due to H_a and H_b are seen at δ 3.47 (dt, J = 4.4 and 6.5 Hz) and δ 3.40 (dd, J = 4.4 and 5.8 Hz), respectively. The small H_a–H_b coupling constant (J = 4.4–4.8 Hz) in the spectra of both 8a and 8d indicates that the relative stereochemistry of the two methine protons is equatorial–axial. Therefore, the ring junction of the cycloadducts 8a and 8d is cis. Because the spectra of the other annulation products, 8b and 8c, also show a small H_a–H_b coupling constant (J = 4–5 Hz), the ring junction in those compounds is also believed to be cis.

The relative stereochemistry of H_b and H_c in 8a-*cis* is believed to be equatorial–axial on the basis of the magnitude of the H_b–H_c coupling constant (J = 5.8 Hz). The cyclohexene ring in 8a-*cis* is hypothesized to exist in two half-chair conformations, as shown in Figure 1. The phenyl group would preferentially occupy the pseudoequatorial position rather than the pseudoaxial, because the strain caused by a 1,3-diaxial interaction between the two phenyl substituents on the cyclohexene ring that would exist in conformer II is believed to be more severe than the allylic strain that would exist in conformer I.[9] Therefore, conformer I would be thermodynamically favored over conformer II. Accordingly, H_a, H_b, and H_c of 8a-*cis* were all believed to be cis relative to each other.

The cis product (8a-*cis*) was converted to a mixture of both geometric isomers (8a-*trans*:8a-*cis* = 5:1) by protonolysis of the intermediate trimethylsilyl enol ether generated from 8a-*cis* by successive treatment with LDA and chlorotrimethylsilane. The two isomers could be separated by TLC on silica gel. Therefore, the initially formed cis derivative 8a-*cis* must be a kinetically controlled product. However, the product ratio cited above does not necessarily reflect the relative thermodynamic stabilities of 8a-*trans* and 8a-*cis*.

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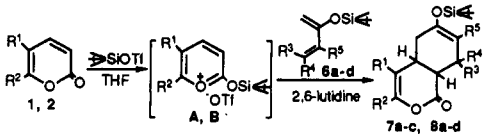
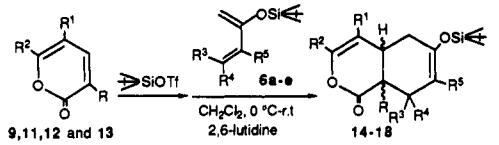
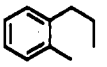
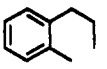
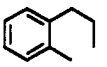
Table II. Diels–Alder Reactions of 1 and 2 with 2-(Trialkylsilyl)oxy Dienes 6a–d



run		reactants R¹	R²		R³	R⁴	R⁵	reaction time (h)	product yield (%)	
1	1	H	Me	6a	H	Ph	H	4	7a	30
2	1	H	Me	6b	H	-(CH₂)₃-		5	7b	35
3	1	H	Me	6c	H	-(CH₂)₄-		3.5	7c	60
4	2	-(CH=CH)₂-		6a	H	Ph	H	3	8a	48
5	2	-(CH=CH)₂-		6b	H	-(CH₂)₃-		3	8b	52
6	2	-(CH=CH)₂-		6c	H	-(CH₂)₄-		2.5	8c	68
7	2	-(CH=CH)₂-		6d	Me	Me	H	5	8d	47

Table III. Diels–Alder Reaction of Activated α-Pyrones 9 and 11–13 with 2-Silyloxy Dienes 6a–e



run		reactant R	R¹	R²		R³	R⁴	R⁵	reaction time (h)	product yield (%)	
1	9a	CO_2Et	-(CH=CH)₂-		6a	H	Ph	H	4	14a	53
2	9b	CO_2Me	-(CH=CH)₂-		6a	H	Ph	H	2.5	15a	80
3	9b	CO_2Me	-(CH=CH)₂-		6b	H	-(CH₂)₃-		3.5	15b	72
4	9b	CO_2Me	-(CH=CH)₂-		6e	H	H	H	3	15e	73
5	11	CO_2Et	-(CH₂)₄-		6a	H	Ph	H	8	16a	57
6	11	CO_2Et	-(CH₂)₄-		6b	H	-(CH₂)₃-		12	16b	48
7	11	CO_2Et	-(CH₂)₄-		6c	H	-(CH₂)₄-		10	16c	62
8	12	CO_2Et	-(CH₂)₃-		6b	H	-(CH₂)₃-		15	17b	30
9	12	CO_2Et	-(CH₂)₃-		6c	H	-(CH₂)₄-		12	17c	40
10	13	CO_2Et			6a	H	Ph	H	4.5	18a	60
11	13	CO_2Et			6c	H	-(CH₂)₄-		6	18c	50
12	13	CO_2Et			6d	Me	Me	H	4	18d	43

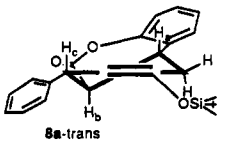


Figure 2.

Because the ring junction in **8a**-*trans* is trans, that compound is incapable of ring inversion.[10] By arguments analogous to those made in connection with the conformation of **8a**-*cis*, the most probable conformation of **8a**-*trans* is that illustrated in Figure 2. In the ^1H NMR spectrum of **8a**-*trans* the signal due to the vinyl proton (R^5) appears at δ 4.85 as a doublet of doublets (J = 2.0 and 0.4 Hz). The signals due to H_a and H_b appear at δ 3.40 (ddd, J = 14.2, 10.9, and 5.3 Hz) and δ 2.70 (dd, J = 14.2 and 9.7 Hz), respectively. The double doublet of doublets at δ 3.40 can be assigned to the axial methine proton (H_a), since it is coupled to the adjacent axial proton (H_b) by a large coupling constant (J = 14.2 Hz) and to the adjacent pseudoaxial and pseudoequatorial protons by coupling constants J = 10.9 and 5.3 Hz, respectively. The upfield shift (δ 2.70) of the H_b proton in the spectrum of **8a**-*trans* relative to its counterpart in **8a**-*cis* (δ 3.40) is a direct consequence of the projection of the proton into a region where it is shielded because of the ring current effect of the benzene ring.

On the other hand, the signal due to the H_b proton of **8b**-*cis* appears at δ 3.10 as a doublet of doublets (J = 4.6 and 8.7 Hz). The splitting of the H_b signal due to coupling between H_b and the adjacent pseudoaxial proton (H_c) is greater for **8b**-*cis* (J_{Hb-Hc} = 8.7 Hz) than for **8a**-*cis* (J_{Hb-Hc} = 5.8 Hz). Although the signals due to H_b and H_c could not be identified in the ^1H NMR spectrum of **8c**-*cis*, the signal due to H_b appeared clearly at δ 3.05 (J = 4.7 and 11.0 Hz) in the spectrum of ketone **19c** (Table IV). Therefore, in both **8b**-*cis* and **8c**-*cis* the relative geometries of H_a and H_b and H_b and H_c are cis and trans, respectively.

Although the relative stereochemistry of the cycloadducts **14–18** could not be established due to the absence of a methine proton that corresponded to H_b of **8a–d** and **19a–c**, the geometry of the newly formed ring junction must be cis, as it is in **8a**-*cis*, to be in accord with the reaction mechanism proposed below.

The cycloadditions described here can be regarded as a kind of ionic Diels–Alder reaction of allyl cations.[11] Therefore, the stereochemistry generated in the cyclo-

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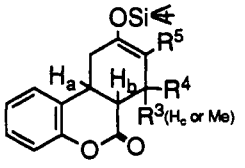
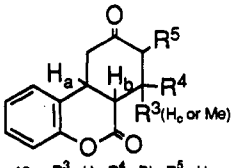
(11) (a) Gassman, P. G.; Singleton, D. A.; Wilwerding, J. J.; Chavan, S. P. *J. Am. Chem. Soc.* **1987**, *107*, 2182 and references therein. (b) Gassman, P. G.; Gorman, D. B. *Ibid.* **1990**, *112*, 8623 and 8624.

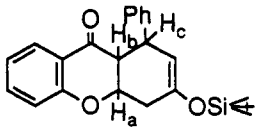
Table IV. Selected Chemical Shifts and Coupling Constants of Cycloadducts 8a–d and Related Compounds



8a : R^3= H_c, R^4= Ph, R^5= H,
8b : R^3= H_c, R^4,R^5= -$(CH_2)_3$-
8c : R^3= H_c, R^4,R^5= -$(CH_2)_4$-
8d : R^3= Me, R^4= Me, R^5= H



19a : R^3= H_c, R^4= Ph, R^5= H,
19b : R^3= H_c, R^4,R^5= -$(CH_2)_3$-
19c : R^3= H_c, R^4,R^5= -$(CH_2)_4$-

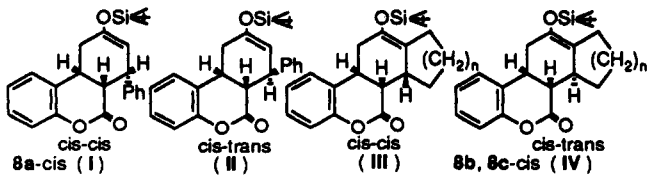


20-cis and 20-trans

compd	relative geometry		chemical shifts and coupling constants in ^{1}H NMR ($CDCl_3$)[a]		
	H_a–H_b	H_b–H_c	H_a	H_b	H_c
8a (**8a**-*cis*)	cis	cis	δ: 3.47	3.40	4.17
			J: dt 4.4, 6.5	dd 4.4, 5.8	dd 3.0, 5.8
(**8a**-*trans*)[b]	trans	trans	δ: 3.40	2.70	4.10
			J: ddd 5.3, 10.9, 14.2	dd 9.7, 14.2	dd 2.0, 9.7
8b (**8b**-*cis*)	cis	trans	δ: 3.32	3.10	
			J: ddd 1.8, 4.6, 10.2	dd 4.6, 8.7	*d*
(**8b**-*trans*)[b]	trans	cis	δ: 3.23	2.75	
			J: ddd 6.4, 10.1, 13.5	dd 6.1, 13.5	*d*
8c (**8c**-*cis*)	cis	trans	*d*	*d*	*d*
8d (**8d**-*cis*)	cis		δ: 3.46	2.70	
			J: dt 4.8, 9.4	d 4.8	
19a[c,e]	cis	cis	δ: 2.62	2.35	3.05
			J: ddd 2.0, 4.7, 14.0	dd 2.0, 5.2	ddd 5.2, 10.7, 12.4
19b[c]	cis	trans	δ: 3.41	3.10	m
			J: dt 5.2, 13.6	dd 5.2, 11.0	
19c[c]	cis	trans	δ: 3.89–3.92	3.05	m
			J: *m*	dd 4.7, 11.0	
20-*cis*[f]	cis	trans	δ: 4.80	2.90	3.95
			J: ddd 0.1, 3.1, 6.4	dd 3.1, 8.7	dd 5.0, 8.7
20-*trans*[f]	trans	cis	δ: 4.60	3.10	4.02
			J: ddd 2.4, 9.2, 13.3	dd 9.2, 13.3	dd 1.5, 9.2

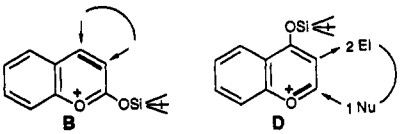
[a] d = doublet, t = triplet, m = multiplet. [b] **8a**- and **8c**-*trans* were obtained by isomerization of **8a**- and **8c**-*cis*. [c] **19a**–**19c** were obtained by desilylation of **8a**–**c**-*cis*. [d] The signals under consideration were behind the multiplet. The geometry of **8c** was estimated from the data of **19c**. [e] In C_6D_6. [f] See ref, 4a.

adducts can easily be explained in terms of a concerted one-step mechanism (a typical Diels–Alder reaction). The (trialkylsilyl)oxy diene can attack the [(trialkylsilyl)-oxy]benzopyrylium cation (B) to yield two possible diastereomers, the products of endo and exo addition. Endo addition to yield I is more favorable than exo addition to yield II because the possibility of a contribution by second-order orbital interactions between the dienophile B and the silyloxy diene **6a** is greater in the former case than in the latter. On the other hand, in the reactions of B with the 2-(trialkylsilyl)oxy dienes **6b,c**, which bear a cyclohexene or cyclopentene ring, endo addition to yield III would be precluded due to steric hindrance in the transition state. Hence, exo addition took place to afford **8b**- and **8c**-*cis* (IV). Therefore, the endo to exo product ratio must reflect a balancing of steric interactions and electronic effects (second-order orbital interactions) during the reaction.



cis-cis **8a**-cis (I) cis-trans (II) cis-cis (III) cis-trans **8b, 8c**-cis (IV)

Earlier we[4a] reported that the reaction of 4-[(trialkylsilyl)oxy]benzopyrylium cation D with benzalacetone (which generates 2-silyloxy diene **6a** in situ) proceeds by a step-by-step mechanism (a double Michael reaction) to afford the annulation product **20**-*cis*. The difference in the reaction mechanisms of the two annulations can be explained by assuming that the 2-[(trialkylsilyl)oxy]-

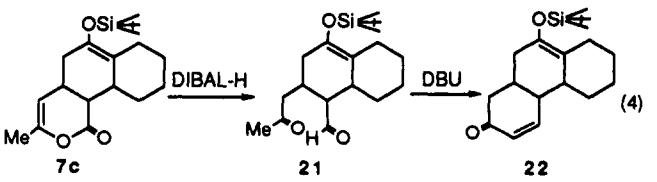


B D

Figure 3. Mode of reaction of B and D. 1Nu and 2El indicate that a nucleophile attacks position 2 initially and an electrophile can react with the resulting silyl enol ether as the second step.

benzopyrylium cation B acted as an electron-deficient dienophile in its cycloadditions to 2-(trialkylsilyl)oxy dienes, whereas the 4-[(trialkylsilyl)oxy]benzopyrylium cation D derived from chromone acted as an oxonium ion in its reactions with 2-(trialkylsilyl)oxy dienes (Figure 3). The reasons for this different behavior are not obvious at the present time.

Transformations of Annulation Products. Reduction of the cycloadduct **7c** with DIBALH gave the aldehyde **21**. Treatment of **21** with DBU[12] gave the cyclic conjugated enone **22** (eq 4).

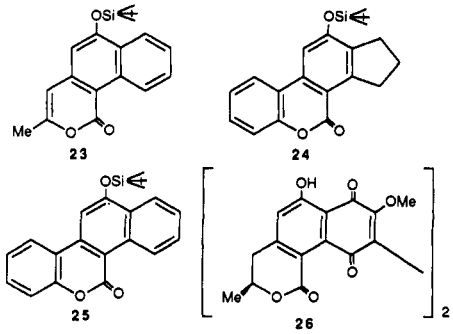


7c **21** **22** (4)

Dehydrogenation of **8c** with DDQ in refluxing toluene gave the benzonaphthopyrone derivative **25** in 80% yield. Similar treatment of **7c** and **8b** afforded **23** and **24** in yields

(12) Nagata, W.; Yoshioka, M.; Terasawa, T. *J. Am. Chem. Soc.* **1972**, *94*, 4672.

of 40 and 50%, respectively. The molecular skeleton of compound **23** makes it a potential intermediate in a synthesis of xanthomegnin (**26**).[13]



Experimental Section

Melting points are uncorrected. Unless otherwise noted, ^1H NMR spectra were recorded at 90 MHz. Flash column chromatography was performed with 230–400-mesh Merck silica gel 60. Thin-layer chromatography (TLC) was performed with Merck silica gel GF-245 plates. *tert*-Butyldimethylsilyl triflate (*t*-BuMe$_2$SiTf) and allyltributylstannane were prepared according to the literature.[14,15] CH_2Cl_2 and 2,6-lutidine were purified by distillation from CaH_2. THF was distilled from sodium benzophenone ketyl. Unless otherwise noted, all other materials were obtained commercially and were used without further purification. All reactions were performed under nitrogen.

Preparation of the 2-[(Trialkylsilyl)oxy]pyrylium Salt A and the 2-[(Trialkylsilyl)oxy]-1-benzopyrylium Salt B. To 6-methyl-2-pyrone (**1**, 0.60 g, 5.45 mmol) or coumarin (**2**, 0.79 g, 5.45 mmol) under N_2, *t*-BuMe$_2$SiTf (1.44 g, 5.45 mmol) was added, drop by drop, by syringe. After addition was complete, the mixture was stirred at 0 °C for 1 h (for the preparation of A) or at 160 °C for 16 h (for the preparation of B). The salt that formed was dissolved in CH_2Cl_2 at room temperature. The solution was then treated with the ketene silyl acetal **3** or the (trialkylsilyl)oxy dienes **6a–c**.

2-[(*tert*-Butyldimethylsilyl)oxy]-6-methylpyrylium triflate (A): ^1H NMR ($CDCl_3$) δ 0.50 (s, 6 H), 1.02 (s, 9 H), 2.43 (d, J = 0.6 Hz, 3 H), 6.59 (dd, J = 9.0, 0.6 Hz, 1 H), 6.69 (dd, J = 7.0, 0.6 Hz, 1 H), 7.91 (dd, J = 9.0, 7.0 Hz, 1 H).

2-[(*tert*-Butyldimethylsilyl)oxy]-1-benzopyrylium triflate (B): ^1H NMR ($CDCl_3$) δ 0.01 (s, 6 H), 1.05 (s, 9 H), 6.81, (d, J = 9.8 Hz, 1 H), 7.50–8.10 (m, 4 H), 8.42 (d, J = 9.8 Hz, 1 H).

Reactions of 2-[(Trialkylsilyl)oxy]pyrylium Salt A and 2-[(Trialkylsilyl)oxy]-1-benzopyrylium Salt B with Ketene Silyl Acetal (3) in the Presence of 2,6-Lutidine. General Procedure. The preparation of **4** is typical. To a CH_2Cl_2 solution (8 mL) of A (derived from **1**, 0.60 g, 5.45 mmol) was added, drop by drop, 2,6-lutidine (0.64 mL, 5.45 mmol) and ketene silyl acetal (**3**, 2.8 g, 11.0 mmol) in CH_2Cl_2 (7 mL) at 0 °C. The mixture was then stirred at room temperature for 4 h. The reaction mixture was poured into ice-cooled 5% aqueous $NaHCO_3$ (50 mL). The mixture was extracted with CH_2Cl_2 (30 mL × 3). The combined extracts were dried ($MgSO_4$) and then concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc (5:1)) to afford 0.56 g (40%) of **4** as a yellow oil.

6-Methyl-4-[(methoxycarbonyl)phenylmethyl]-3,4-dihydro-2*H*-pyran-2-one (4): yellow oil, 0.56 g (40%); ^1H NMR ($CDCl_3$) δ 1.82 (s, 3 H), 2.20–2.80 (m, 2 H), 3.00–3.41 (m, 1 H), 3.39 (d, J = 11.0 Hz, 1 H), 3.67 (s, 3 H), 5.11 (dd, J = 4.4, 0.4 Hz, 1 H), 7.20–7.35 (m, 5 H); MS m/z M$^+$ 260 (100), M$^+$ + 1 (50).

4-[(Methoxycarbonyl)phenylmethyl]-3,4-dihydro-2*H*-benzopyran-2-one (5): colorless crystals, 0.75 g (80%); mp 106–107 °C; IR (KBr, cm^{-1}) 1710, 1410, 1200, 1180; ^1H NMR ($CDCl_3$) δ 2.53–2.58 (m, 2 H), 3.50 (s, 3 H), 3.60–3.81 (m, 2 H), 6.91–7.41 (m, 9 H); MS m/z M$^+$ 296 (70), M$^+$ + 1 (20), 265 (25), 237 (90), 165 (100). Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.95; H, 5.44. Found: C, 73.13; H, 5.45.

General Procedure for 2-(*tert*-Butyldimethylsilyl)oxy Dienes (6a–d). The preparation of **6a** is typical. To a suspension of lithium diisopropylamide (LDA, 75.0 mmol) in dry THF (70 mL) was added a solution of benzalacetone (10.4 g, 70.9 mmol) in THF (30 mL) at −78 °C. After the mixture was stirred for 30 min at −78 °C, *t*-BuMe$_2$SiCl (16.0 g, 0.106 mmol) in THF (50 mL) was added drop by drop. The mixture was refluxed for 5 h and then was allowed to cool to room temperature over 3 h. Most of the THF was evaporated in vacuo. Hexane (100 mL) was added, and the mixture was filtered through Celite. Concentration of the filtrate in vacuo left an oily residue. Distillation gave **6a** as a pale yellow oil (13.3 g, 72%), bp 124–126 °C (0.67 mmHg).

2-[(*tert*-Butyldimethylsilyl)oxy]-4-phenyl-1,3-butadiene (6a): pale yellow oil, 13.3 g (72%); bp 124–126 °C (0.6 mmHg); ^1H NMR ($CDCl_3$) δ 0.15 (s, 6 H), 0.95 (s, 9 H), 4.35 (d, J = 1.76 Hz, 2 H), 6.47 (d, J = 15.8 Hz, 1 H), 6.81 (d, J = 15.8 Hz, 1 H), 7.10–7.50 (m, 5 H); MS m/z M$^+$ 260 (80), M$^+$ + 1 (40), 245 (100).

1-(1-Cyclopentenyl)-1-[(*tert*-butyldimethylsilyl)oxy]ethene (6b): colorless oil, 8.5 g (52%); bp 52–53 °C (0.06 mmHg); ^1H NMR ($CDCl_3$) δ 0.19 (s, 6 H), 0.99 (s, 9 H), 1.90–2.10 (m, 2 H), 2.40–2.60 (m, 4 H), 4.28 (br s, 2 H), 6.01 (s, 1 H); MS m/z M$^+$ 224 (80), M$^+$ + 1 (50), 209 (100).

1-(1-Cyclohexenyl)-1-[(*tert*-butyldimethylsilyl)oxy]ethene (6c): colorless oil, 10.3 g (56%); bp 74–76 °C (0.05 mmHg); ^1H NMR ($CDCl_3$) δ 0.28 (s, 6 H), 0.80 (s, 9 H), 1.50–1.80 (m, 4 H), 2.00–2.20 (m, 4 H), 4.12 (s, 1 H), 4.27 (s, 1 H), 6.10–6.20 (m, 1 H); MS m/z M$^+$ 238 (80), M$^+$ + 1 (50), 223 (100).

2-[(*tert*-Butyldimethylsilyl)oxy]-4,4-dimethyl-1,3-butadiene (6d): colorless oil, 12.8 g (79%); bp 54–56 °C (0.15 mmHg); ^1H NMR ($CDCl_3$) δ 0.19 (s, 6 H), 0.97 (s, 9 H), 1.97 (s, 3 H), 1.92 (s, 3 H), 4.18 (s, 1 H), 4.33 (s, 1 H), 5.59 (br s, 1 H); MS m/z M$^+$ 212 (30), M$^+$ + 1 (15), 197 (100).

(Trimethylsilyl)oxy diene **6e** was prepared as previously described.[16]

Reaction of 1 and 2 with (Trialkylsilyl)oxy Dienes 6a–d in the Presence of 2,6-Lutidine and *tert*-Butyldimethylsilyl Triflate. General Procedure (Table II). The preparation of **8a** is typical. To a solution of **2** (0.85 g, 5.82 mmol) in THF (10 mL) was added, drop by drop, *t*-BuMe$_2$SiTf (1.34 mL, 5.82 mmol) at room temperature. After the mixture was stirred for 1 h, 2,6-lutidine (0.7 mL, 5.82 mmol) and (trialkylsilyl)oxy diene **6a** (3.20 g, 11.6 mmol) in THF (7 mL) was added at 0 °C. The mixture was stirred for 3 h at room temperature and then was poured into ice-cooled 5% aqueous $NaHCO_3$ (50 mL). The mixture was extracted with CH_2Cl_2 (30 mL × 3). The combined extracts were dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc (5:1)) to afford 1.14 g (48%) of **8a** as crystalline solids.

6-[(*tert*-Butyldimethylsilyl)oxy]-3-methyl-8-phenyl-4a,5,8,8a-tetrahydro-1*H*-benzopyran-1-one (7a): yellow oil, 0.23 g (30%); IR (neat, cm^{-1}) 2950, 1755, 1710, 1650; ^1H NMR ($CDCl_3$) δ 0.15 (s, 6 H), 0.85 (s, 9 H), 1.21 (s, 3 H), 1.90–2.50 (m, 2 H), 2.80–3.37 (m, 2 H), 3.73–3.92 (br m, 1 H), 4.75 (dd, J = 3.5, 1.3 Hz, 1 H), 4.97 (dd, J = 3.7, 1.0 Hz, 1 H), 7.00–7.30 (m, 5 H); MS m/z M$^+$ 370 (70), M$^+$ + 1 (25), 342 (30), 327 (50), 260 (100). This cycloadduct was readily desilylated by exposure to atmospheric moisture or to silica gel to give the corresponding ketone **7a′**. **7a′**: colorless crystals; mp 147–148 °C; ^1H NMR ($CDCl_3$) δ 1.86 (s, 3 H), 2.50–3.00 (m, 4 H), 3.20–4.00 (m, 3 H), 5.14 (dd, J = 6.2, 1.3 Hz, 1 H), 7.10–7.40 (m, 5 H); MS m/z M$^+$ 256 (70), M$^+$ + 1 (50), 151 (15), 199 (100); HRMS m/z calcd for $C_{16}H_{16}O_3$ 256.1098, found 256.1085.

6-[(*tert*-Butyldimethylsilyl)oxy]-7,8-trimethylene-3-methyl-4a,5,8,8a-tetrahydro-1*H*-benzopyran-1-one (7b): yellow oil, 0.18 g (35%); IR (neat, cm^{-1}) 2980, 1760, 1710, 1660; ^1H NMR ($CDCl_3$) δ 0.20 (s, 3 H), 0.25 (s, 3 H), 0.94 (s, 9 H), 1.90 (s, 3 H), 1.20–3.00 (br m, 11 H), 5.25 (dd, J = 5.9, 1.3 Hz, 1 H);

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(15) (a) Rosenberg, S. D.; Gibbons, A. J., Jr.; Ramsden, H. E. *J. Am. Chem. Soc.* **1957**, *79*, 2137. (b) Seyferth, D.; Weiner, M. A. *J. Org. Chem.* **1961**, *26*, 4797.

(16) Jung, M. E.; McCombs, C. A. *Tetrahedron Lett.* **1976**, *34*, 2935.

MS m/z M^+ 334 (100), $M^+ + 1$ (60), 319 (25), 291 (30).

6-[(*tert*-Butyldimethylsilyl)oxy]-3-methyl-4a,5,7,8,9,10,-10a,10b-octahydro-1*H*-naphtho[1,2-*c*]pyran-1-one (7c): yellow oil, 2.10 g (60%); IR (neat, cm^{-1}) 2960, 1770, 1690, 1660, 1180; ^1H NMR ($CDCl_3$) δ 0.15 (s, 6 H), 0.95 (s, 9 H), 1.84 (s, 3 H), 1.10–2.97 (br m, 13 H), 5.00 (d, J = 4.7 Hz, 1 H); MS m/z M^+ 348 (80), $M^+ + 1$ (50), 293 (70), 291 (100).

9-[(*tert*-Butyldimethylsilyl)oxy]-7-phenyl-6a,7,10,10a-tetrahydro-6*H*-dibenzo[*b*,*d*]pyran-6-one (8a-*cis*): crystalline solids, 1.14 g (48%); IR (neat, cm^{-1}) 2955, 1760, 1500, 1100; ^1H NMR ($CDCl_3$) δ 0.24 (s, 6 H), 1.07 (s, 9 H), 2.44–2.58 (m, 2 H), 3.40 (dd, J = 5.8, 4.4 Hz, 1 H), 3.47 (dt, J = 6.5, 4.4 Hz, 1 H), 4.17 (dd, J = 5.8, 3.0 Hz, 1 H), 5.20 (dt, J = 3.0, 1.5 Hz, 1 H), 6.60–7.25 (m, 9 H); MS m/z M^+ 406 (100), $M^+ + 1$ (30), 363 (80), 349 (70); HRMS m/z calcd for $C_{25}H_{30}O_3Si$ 406.1962, found 406.1960.

11-[(*tert*-Butyldimethylsilyl)oxy]-1,2,3,3a,3b,4,9b,10-octahydrobenz[*b*]indeno[5,4-*d*]pyran-4-one or 12-[(*tert*-Butyldimethylsilyl)oxy]-6-oxaestra-1,3,5(10),12(13)-tetraen-7-one (8b-*cis*): crystalline solids, 0.96 g (52%); ^1H NMR ($CDCl_3$) δ 0.15 (s, 3 H), 0.17 (s, 3 H), 0.97 (s, 9 H), 1.50–2.90 (br m, 9 H), 3.10 (dd, J = 8.7, 4.6 Hz, 1 H), 3.32 (ddd, J = 1.8, 4.6, 10.2 Hz, 1 H), 6.98–7.35 (m, 4 H); MS m/z M^+ 370 (100), $M^+ + 1$ (30), 313 (40), 285 (20), 254 (33); HRMS m/z calcd for $C_{22}H_{30}O_3Si$ 370.1965, found 370.1990.

Isomerization of 8a-*cis* and 8b-*cis* by Treatment with LDA. General Procedure. The isomerization of 8a-*cis* is typical. To a suspension of LDA (1.80 mmol) in dry THF (5 mL) was added a solution of 8a-*cis* (0.73 g, 1.80 mmol) in THF (3 mL) at −78 °C. After the mixture was stirred for 30 min at −78 °C, Me_3SiCl (0.3 mL, 2.34 mmol) was added drop by drop. After 30 min, the reaction was quenched with 5% aqueous HCl (15 mL). The mixture was stirred for 40 min at room temperature. The mixture was then diluted with CH_2Cl_2 (30 mL) and was washed with water (20 mL × 2). The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by TLC (hexane/EtOAc (5:1)) to give 0.07 g (10%) of 8a-*cis* and 0.40 g (55%) of 8a-*trans*. 8a-*trans*: crystalline solids; ^1H NMR ($CDCl_3$) δ 0.20 (s, 6 H), 1.00 (s, 9 H), 2.70 (dd, J = 14.2, 9.7 Hz, 1 H), 2.45–3.03 (m, 2 H), 3.40 (ddd, J = 14.2, 10.9, 5.3 Hz, 1 H), 4.10 (dd, J = 9.7, 2.0 Hz, 1 H), 4.85 (dd, J = 2.0, 0.4 Hz, 1 H), 6.92–7.45 (m, 9 H); MS m/z M^+ 406 (100), $M^+ + 1$ (50); HRMS m/z calcd for $C_{25}H_{30}O_3Si$ 406.1952, found 406.1949.

8b-*trans*: colorless oil, 0.57 g (43%); ^1H NMR ($CDCl_3$, 500 MHz) δ 0.15 (s, 3 H), 0.17 (s, 3 H), 0.96 (s, 9 H), 1.05–2.65 (m, 9 H), 2.75 (dd, J = 13.5, 6.1 Hz, 1 H), 3.23 (ddd, J = 13.5, 10.1, 6.4 Hz, 1 H), 7.00–7.31 (m, 4 H); HRMS m/z calcd for $C_{22}H_{30}O_3Si$ 370.1962, found 370.1937.

12-[(*tert*-Butyldimethylsilyl)oxy]-1,2,3,4,4a,4b,10b,11-octahydro-5*H*-benzo[*b*]naphtho[2,1-*d*]pyran-5-one (8c): colorless crystals, 1.08 g (68%); mp 107–109 °C; IR (KBr, cm^{-1}) 2960, 1767, 1485, 1070; ^1H NMR ($CDCl_3$) δ 0.10 (s, 3 H), 0.11 (s, 3 H), 0.93 (s, 9 H), 1.10–2.98 (br m, 12 H), 3.10–3.25 (m, 1 H), 6.90–7.25 (m, 4 H); MS m/z M^+ 384 (30), $M^+ + 1$ (15), 380 (70), 342 (100), 323 (80). Anal. Calcd for $C_{23}H_{32}O_3Si$: C, 71.82; H, 8.38. Found: C, 71.57; H, 8.65.

9-[(*tert*-Butyldimethylsilyl)oxy]-7,7-dimethyl-6a,7,10,10a-tetrahydro-6*H*-dibenzo[*b*,*d*]pyran-6-one (8d): colorless oil, 0.56 g (47%); IR (neat, cm^{-1}) 2950, 1762, 1480, 1050; ^1H NMR ($CDCl_3$) δ 0.15 (s, 3 H), 0.18 (s, 3 H), 0.95 (s, 9 H), 1.18 (s, 3 H), 1.30 (s, 3 H), 2.28–2.50 (m, 2 H), 2.70 (d, J = 4.8 Hz, 1 H), 3.46 (dt, J = 9.4, 4.8 Hz, 1 H), 4.70 (d, J = 0.4 Hz, 1 H), 6.90–7.40 (m, 4 H); MS m/z M^+ 358 (80), $M^+ + 1$ (35), 343 (100), 301 (70); HRMS m/z calcd for $C_{21}H_{30}O_3Si$ 358.1962, found 358.1949.

Reaction of 9a,b with Allyltributylstannane. General Procedure. The preparation of 10a is typical. To a solution of 9a (0.70 g, 3.21 mmol) in CH_2Cl_2 (6 mL) was added, drop by drop, *t*-$BuMe_2SiTf$ (0.74 mL, 3.21 mmol) at room temperature. After the mixture was stirred for 30 min, a solution of 2,6-lutidine (0.37 mL, 3.21 mmol) and allyltributylstannane (1.91 g, 5.78 mmol) in CH_2Cl_2 (3 mL) was added at 0 °C. The mixture was stirred for 5 h at room temperature, then was poured into ice-cooled 5% aqueous $NaHCO_3$ (50 mL). The mixture was extracted with CH_2Cl_2 (30 mL × 3). The combined extracts were dried ($MgSO_4$), filtered, and concentrated in vacuo to give a yellow oil. Flash column chromatography on silica gel (hexane/EtOAc (5:1)) gave 0.38 g (45%) of 10a as a colorless oil.

4-Allyl-3-(ethoxycarbonyl)-3,4-dihydro-2*H*-benzopyran-2-one (10a): colorless oil, 0.38 g (45%); ^1H NMR ($CDCl_3$) δ 1.05 (t, J = 7.2 Hz, 3 H), 2.30–2.60 (m, 2 H), 3.46 (ddd, J = 7.9, 6.8, 2.9 Hz, 1 H), 3.83 (d, J = 2.9 Hz, 1 H), 4.10 (q, J = 7.2 Hz, 2 H), 5.00–5.30 (m, 2 H), 5.50–6.10 (m, 1 H), 7.00–7.45 (m, 4 H); MS m/z M^+ 260 (80), $M^+ + 1$ (28), 219 (100), 215 (85); HRMS m/z calcd for $C_{15}H_{16}O_4$ 260.1049, found 260.1055.

4-Allyl-3-(methoxycarbonyl)-3,4-dihydro-2*H*-benzopyran-2-one (10b): colorless oil, 0.45 g (60%); ^1H NMR ($CDCl_3$) δ 2.30–2.52 (m, 2 H), 3.49 (ddd, J = 7.9, 6.6, 3.1 Hz, 1 H), 3.61 (s, 3 H), 3.85 (d, J = 3.1 Hz, 1 H), 5.06–5.35 (m, 2 H), 5.58–6.05 (m, 1 H), 7.06–7.45 (m, 4 H); MS m/z M^+ 246; HRMS m/z calcd for $C_{14}H_{14}O_4$ 246.0893, found 246.0894.

Reaction of 9a,b and 11–13 with (Trialkylsilyl)oxy Dienes 6a–e in the Presence of *tert*-Butyldimethylsilyl Triflate and 2,6-Lutidine. General Procedure (Table III). The preparation of 16a is typical. To a solution of 11 (1.50 g, 6.75 mmol) in CH_2Cl_2 (10 mL) was added, drop by drop, *t*-$BuMe_2SiTf$ (1.56 mL, 6.75 mmol) at room temperature. After the mixture was stirred for 30 min, a solution of 2,6-lutidine (0.79 mL, 6.75 mmol) and the (trialkylsilyl)oxy diene (6a, 2.8 g, 10.2 mmol) in CH_2Cl_2 (7 mL) was added at 0 °C. The mixture was stirred for 8 h at room temperature and then was poured into ice-cooled 5% aqueous $NaHCO_3$ (30 mL). The mixture was extracted with CH_2Cl_2 (30 mL × 3). The combined extracts were dried ($MgSO_4$) and then concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc (5:1)) to afford 1.85 g (57%) of 16a as crystalline solids.

9-[(*tert*-Butyldimethylsilyl)oxy]-6a-(ethoxycarbonyl)-7-phenyl-6a,7,10,10a-tetrahydro-6*H*-dibenzo[*b*,*d*]pyran-6-one (14a): colorless crystals, 1.07 g (53%); mp 142–143 °C; ^1H NMR ($CDCl_3$) δ 0.29 (s, 6 H), 1.02 (s, 9 H), 1.10 (t, J = 7.0 Hz, 3 H), 2.46–2.62 (m, 2 H), 3.85–4.25 (m, 3 H), 4.48 (d, J = 2.6 Hz, 1 H), 5.18 (d, J = 2.6 Hz, 1 H), 6.75–7.48 (m, 9 H); MS m/z M^+ 478 (30), 470 (100), 421 (20), 405 (80), 387 (70). Anal. Calcd for $C_{28}H_{34}O_5Si$: C, 70.25; H, 7.16. Found: C, 69.89; H, 7.30.

9-[(*tert*-Butyldimethylsilyl)oxy]-6a-(methoxycarbonyl)-7-phenyl-6a,7,10,10a-tetrahydro-6*H*-dibenzo[*b*,*d*]pyran-6-one (15a): colorless crystals, 2.45 g (80%); mp 153–155 °C; ^1H NMR ($CDCl_3$) δ 0.17 (s, 6 H), 1.00 (s, 9 H), 2.45–2.55 (br m, 2 H), 3.60 (s, 3 H), 3.85 (t, J = 7.0 Hz, 1 H), 4.50 (d, J = 1.6 Hz, 1 H), 5.10 (d, J = 1.6 Hz, 1 H), 6.45–7.26 (m, 9 H); MS m/z M^+ 464 (30), 446 (100), 408 (35), 406 (50). Anal. Calcd for $C_{27}H_{32}O_5Si$: C, 67.79; H, 6.94. Found: C, 67.90; H, 7.13.

11-[(*tert*-Butyldimethylsilyl)oxy]-3b-(methoxycarbonyl)-1,2,3,3a,3b,4,9b,10-octahydrobenz[*b*]indeno[5,4-*d*]pyran-4-one or 2-[(*tert*-Butyldimethylsilyl)oxy]-8-(methoxycarbonyl)-6-oxaestra-1,3,5(10),12(13)-tetraen-7-one (15b): colorless oil, 0.95 g (72%); ^1H NMR ($CDCl_3$) δ 0.21 (s, 3 H), 0.25 (s, 3 H), 1.00 (s, 9 H), 1.32–2.90 (br m, 9 H), 3.20–3.40 (br m, 1 H), 3.80 (s, 3 H), 7.20–7.45 (m, 4 H); MS m/z M^+ 428 (100), $M^+ + 1$ (70), 369 (50), 311 (15); HRMS m/z calcd for $C_{24}H_{32}O_5Si$ 428.2019, found 428.2034.

9-[(*tert*-Butyldimethylsilyl)oxy]-6a-(methoxycarbonyl)-6a,7,10,10a-tetrahydro-6*H*-dibenzo[*b*,*d*]pyran-6-one (15e): crystalline solids, 0.55 g (73%); ^1H NMR ($CDCl_3$) δ 0.28 (s, 3 H), 0.30 (s, 3 H), 1.05 (s, 9 H), 2.30–2.95 (br m, 3 H), 3.13 (dd, J = 10.5, 4.9 Hz, 1 H), 3.70 (s, 3 H), 3.75 (dd, J = 6.7, 4.0 Hz, 1 H), 5.03 (dd, J = 0.9, 5.2 Hz, 1 H), 7.10–7.45 (m, 4 H); MS m/z M^+ 388 (80), $M^+ + 1$ (30), 357 (25), 331 (70), 329 (100); HRMS m/z calcd for $C_{21}H_{28}O_5Si$ 388.1707, found 388.1712.

9-[(*tert*-Butyldimethylsilyl)oxy]-6a-(ethoxycarbonyl)-7-phenyl-1,2,3,4,6a,7,10,10a-octahydro-6*H*-dibenzo[*b*,*d*]-pyran-6-one (16a): crystalline solids, 1.85 g (57%); ^1H NMR ($CDCl_3$) δ 0.25 (s, 6 H), 0.95 (s, 9 H), 1.20 (t, J = 7.0 Hz, 3 H), 1.50–2.50 (br m, 10 H), 3.15 (t, J = 7.9 Hz, 1 H), 4.00–4.30 (m, 2 H), 4.35 (d, J = 2.7 Hz, 1 H), 5.08 (d, J = 2.7 Hz, 1 H), 7.27–7.48 (m, 5 H); HRMS m/z calcd for $C_{28}H_{38}O_5Si$ 482.2498, found 482.2510.

11-[(*tert*-Butyldimethylsilyl)oxy]-3b-(ethoxycarbonyl)-1,2,3,3a,3b,4,6,7,8,9,9b,10-dodecahydrobenz[*b*]indeno[5,4-*d*]-pyran-4-one or 12-[(*tert*-Butyldimethylsilyl)oxy]-8-(ethoxycarbonyl)-6-oxaestra-5(10),12(13)-dien-7-one (16b): colorless oil, 0.87 g (48%); IR (neat, cm^{-1}) 1775, 1669, 1463, 1294; ^1H NMR ($CDCl_3$) δ 0.06 (s, 6 H), 0.87 (s, 9 H), 1.20 (t, J = 7.1

Hz, 3 H), 1.50–2.80 (br m, 17 H), 3.30–3.40 (m, 1 H), 4.02–4.30 (m, 2 H); MS *m/z* M^+ 446 (100), $M^+ + 1$ (70), 431 (10), 389 (80).

12-[(*tert*-Butyldimethylsilyl)oxy]-4b-(ethoxycarbonyl)-1,2,3,4,4a,4b,7,8,9,10,10b,11-dodecahydro-5*H*-benzo[*b*]naphtho[2,1-*d*]pyran-5-one (16c): crystalline solids, 1.47 g (62%); ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 6 H), 0.97 (s, 9 H), 1.25 (t, *J* = 7.0 Hz, 3 H), 1.40–2.98 (br m, 20 H), 4.05–4.35 (m, 2 H); MS *m/z* M^+ 460 (20), 457 (100); HRMS *m/z* calcd for $C_{28}H_{40}O_5Si$ 460.2644, found 460.2629.

10-[(*tert*-Butyldimethylsilyl)oxy]-3b-(ethoxycarbonyl)-2,3,3a,3b,4,6,7,8,8b,9-decahydro-1*H*-cyclopent[*b*]indeno[5,4-*d*]pyran-4-one (17b): colorless oil, 0.57 g (30%); ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 6 H), 0.95 (s, 9 H), 1.30 (t, *J* = 7.0 Hz, 3 H), 1.55–3.20 (br m, 16 H), 4.10–4.37 (m, 2 H); MS *m/z* M^+ 432 (80), $M^+ + 1$ (60), 404 (15), 387 (30), 359 (70), 321 (100); HRMS *m/z* calcd for $C_{24}H_{36}O_5Si$ 432.2332, found 432.2343.

11-[(*tert*-Butyldimethylsilyl)oxy]-4b-(ethoxycarbonyl)-1,2,3,4,4a,4b,5,7,8,9,9b,10-dodecahydrocyclopenta[*b*]naphtho[1,2-*d*]pyran-5-one (17c): colorless oil, 0.45 g (40%); IR (neat, cm^{-1}) 1790, 1730, 1670, 1460; ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 6 H), 0.90 (s, 9 H), 1.25 (t, *J* = 7.0 Hz, 3 H), 1.50–3.20 (br m, 18 H), 4.10–4.45 (m, 2 H); MS *m/z* M^+ 446 (80), $M^+ + 1$ (50), 418 (15), 373 (100), 401 (20); HRMS *m/z* calcd for $C_{25}H_{38}O_5Si$ 446.2487, found 446.2467.

9-[(*tert*-Butyldimethylsilyl)oxy]-6a-(ethoxycarbonyl)-7-phenyl-6a,7,10,10a,11,12-hexahydro-6*H*-benzo[*d*]naphtho[1,2-*b*]pyran-6-one (18a): colorless crystals, 1.88 g (60%); mp 152–154 °C; ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 6 H), 0.95 (s, 9 H), 0.97 (t, *J* = 7.2 Hz, 3 H), 2.10–3.00 (br m, 6 H), 3.20 (dd, *J* = 7.2, 10.3 Hz, 1 H), 3.75–4.12 (m, 2 H), 4.20–4.33 (br s, 1 H), 5.15 (br s, 1 H), 7.03–7.50 (m, 9 H); MS *m/z* M^+ 530 (30), $M^+ + 1$ (10), 457 (100), 427 (80). Anal. Calcd for $C_{32}H_{38}O_5Si$: C, 72.46; H, 7.21. Found: C, 72.60; H, 7.40.

11-[(*tert*-Butyldimethylsilyl)oxy]-6a-(ethoxycarbonyl)-6a,6b,7,8,9,10,12,12a,13,14-decahydro-6*H*-dinaphtho[1,2-*b*:2′,1′-*d*]pyran-6-one (18c): yellow oil, 1.56 g (50%); IR (neat, cm^{-1}) 2930, 1775, 1730, 1460; ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 6 H), 1.07 (s, 9 H), 1.20 (t, *J* = 7.0 Hz, 3 H), 1.30–3.18 (br m, 16 H), 4.10–4.44 (m, 2 H), 7.00–7.70 (m, 4 H); MS *m/z* M^+ 508; HRMS *m/z* calcd for $C_{30}H_{40}O_5Si$ 508.2645, found 508.2651.

9-[(*tert*-Butyldimethylsilyl)oxy]-7,7-dimethyl-6a-(ethoxycarbonyl)-6a,7,10,10a,11,12-hexahydro-6*H*-benzo[*d*]naphtho[1,2-*b*]pyran-6-one (18d): colorless oil, 0.36 g (43%); ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 3 H), 0.25 (s, 3 H), 0.90 (s, 9 H), 1.00 (t, *J* = 7.2 Hz, 3 H), 1.40 (s, 3 H), 1.67 (s, 3 H), 2.10–2.90 (br m, 6 H), 3.06 (dd, *J* = 3.4, 9.5 Hz, 1 H), 3.97–4.30 (m, 2 H), 5.65 (s, 1 H), 7.10–7.55 (m, 4 H); MS *m/z* M^+ 482 (70), $M^+ + 1$ (40), 425 (60), 409 (100); HRMS *m/z* calcd for $C_{28}H_{38}O_5Si$ 482.2487, found 482.2450.

Desilylation of 8a-*cis*, 8b-*cis*, and 8c. Ketone derivatives **19a–c** were easily obtained from **8a-*cis***, **8b-*cis***, and **8c**, respectively, by treatment with TBAF in THF at −78 °C and subsequent protonolysis with dilute aqueous HCl.

6a,7,8,9,10,10a-Hexahydro-6*H*-dibenzo[*b*,*d*]pyran-6,9-dione (19a): colorless crystals, 0.21 g (75%); mp 167–169 °C; ^{1}H NMR (C_6D_6, 500 MHz) δ 1.72–2.43 (m, 4 H), 2.35 (dd, *J* = 5.2, 2.0 Hz, 1 H), 2.62 (ddd, *J* = 14.0, 4.7, 2.0 Hz, 1 H), 3.05 (ddd, *J* = 12.4, 10.7, 5.2 Hz, 1 H), 6.50–7.20 (m, 9 H); HRMS *m/z* calcd for $C_{19}H_{16}O_3$ 292.1089, found 292.1103.

1,2,3,3a,3b,4,9b,10,11,11a-Decahydrobenz[*b*]indeno[5,4-*d*]pyran-4,11-dione (19b): crystalline solids, 0.10 g (65%); ^{1}H NMR ($CDCl_3$, 500 MHz) 1.53–2.97 (m, 10 H), 3.10 (dd, *J* = 11.0, 5.2 Hz, 1 H), 3.41 (dt, *J* = 13.6, 5.2 Hz, 1 H), 7.00–7.40 (m, 4 H); HRMS *m/z* calcd for $C_{16}H_{16}O_3$ 256.1100, found 256.1120.

1,2,3,4,4a,4b,10b,11,12,12a-Decahydro-5*H*-benzo[*b*]naphtho[2,1-*d*]pyran-5,12-dione (19c): colorless crystals, 0.25 g (60%); mp 138–140 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.02–2.30 (m, 9 H), 2.08 (ddd, *J* = 11.5, 8.5, 2.9 Hz, 1 H), 2.78 (dd, *J* = 15.0, 4.7 Hz, 1 H), 3.05 (dd, *J* = 11.0, 4.7 Hz, 1 H), 3.12 (dd, *J* = 15.0, 3.5 Hz, 1 H), 3.89–3.92 (m, 1 H), 7.00–7.40 (m, 4 H); MS *m/z* M^+ 270 (80), $M^+ + 1$ (50), 252 (15), 242 (100), 227 (40). Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.32; H, 6.91.

Reduction of 7c with DIBALH. To a solution **7c** (2.14 g, 6.51 mmol) in dry Et_2O (15 mL) at −78 °C was added *i*-Bu_2AlH (6.70 mmol, 6.70 mL of 1 *M* solution in hexane). The mixture was stirred for 3 h at −78 °C, and then the reaction was quenched with MeOH (10 mL). The mixture was filtered through Celite. The filtrate was extracted with CH_2Cl_2 (30 mL × 3). The extracts were concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc (5:1)) to give 1.87 g (80%) of **21** as a pale yellow oil: IR (neat, cm^{-1}) 2930, 1720, 1670; ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 6 H), 0.97 (s, 9 H), 1.10–3.14 (br m, 15 H), 2.20 (s, 3 H), 9.77 (d, *J* = 4.8 Hz, 1 H); MS *m/z* M^+ 350 (100), $M^+ + 1$ (35), $M^+ + 2$ (20), 334 (15), 322 (100); HRMS *m/z* calcd for $C_{20}H_{34}O_3Si$ 350.2279, found 350.2265.

9-[(*tert*-Butyldimethylsilyl)oxy]-1,2,4a,4b,5,6,7,8,10,10a-decahydrophenanthren-2-one (22). To a solution of aldehyde **21** (1.52 g, 4.32 mmol) in dry Et_2O (8 mL) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.66 mL, 4.40 mmol). The mixture was refluxed for 4 h. After being cooled, the mixture was diluted with water. The two liquid layers were separated. The aqueous layer was extracted with CH_2Cl_2 (20 mL × 3). The combined organic layers were dried ($MgSO_4$) and then concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc (5:1)) to give 0.29 g (20%) of **22** as a pale yellow oil: IR (neat, cm^{-1}) 2920, 1670; ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 6 H), 1.00 (s, 9 H), 1.10–3.50 (br m, 15 H), 6.00 (dd, *J* = 10.0, 0.6 Hz, 1 H), 6.95 (d, *J* = 10.0 Hz, 1 H); MS *m/z* M^+ 332 (80), $M^+ + 1$ (70), 317 (20), 257 (100); HRMS *m/z* calcd for $C_{20}H_{32}O_2Si$ 332.2168, found 332.2183.

Dehydrogenation of 7c, 8b, and 8c. General Procedure. The dehydrogenation of **8c** is typical. To a solution of **8c** (1.60 g, 4.17 mmol) in toluene (10 mL) was added 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ, 3.80 g, 16.7 mmol). The mixture was refluxed for 5 h. After being cooled, the mixture was filtered through Celite and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc (3:1)) to give 1.22 g (80%) of **25** as colorless crystals.

6-[(*tert*-Butyldimethylsilyl)oxy]-3-methyl-1*H*-naphtho[1,2-*c*]pyran-1-one (23): colorless crystals, 0.25 g (40%); mp 141–142 °C; IR (KBr, cm^{-1}) 2930, 1710, 1590, 1410, 1250, 1130; ^{1}H NMR ($CDCl_3$) δ 0.39 (s, 6 H), 1.13 (s, 9 H), 2.30 (s, 3 H), 6.24 (s, 1 H), 6.60 (s, 1 H), 7.45–7.80 (m, 2 H), 8.25 (dd, *J* = 8.1, 1.8 Hz, 1 H), 9.70 (dd, *J* = 8.1, 1.3 Hz, 1 H); MS *m/z* M^+ 340 (85), $M^+ + 1$ (70), 325 (15), 283 (100). Anal. Calcd for $C_{20}H_{24}O_3Si$: C, 70.55; H, 7.11. Found: C, 70.76; H, 7.29.

11-[(*tert*-Butyldimethylsilyl)oxy]-1,2,3-trihydrobenz[*b*]indeno[5,4-*d*]pyran-4-one or 12-[(*tert*-Butyldimethylsilyl)oxy]-6-oxaestra-1,3,5(10),8(9),11,13(14)-hexaen-7-one (24): colorless crystals, 0.32 g (50%); mp 144–146 °C; ^{1}H NMR ($CDCl_3$) δ 0.36 (s, 6 H), 1.10 (s, 9 H), 2.03–2.45 (m, 2 H), 2.85–3.05 (m, 2 H), 3.40–3.60 (m, 2 H), 4.05 (s, 1 H), 7.20–7.95 (m, 4 H); MS *m/z* M^+ 366 (50), $M^+ + 1$ (15), 364 (40), 309 (100), 307 (80). Anal. Calcd for $C_{22}H_{26}O_3Si$: C, 72.09; H, 7.15. Found: C, 72.37; H, 7.35.

12-[(*tert*-Butyldimethylsilyl)oxy]-5*H*-benzo[*b*]naphtho[2,1-*d*]pyran-5-one (25): colorless crystals, 1.22 g (80%); mp 158–160 °C; ^{1}H NMR ($CDCl_3$) δ 0.45 (s, 6 H), 1.20 (s, 9 H), 7.20–7.83 (m, 6 H), 7.95 (dd, *J* = 7.2, 0.4 Hz, 1 H), 8.30 (dd, *J* = 6.8, 0.8 Hz, 1 H), 9.75 (dd, *J* = 7.2, 0.4 Hz, 1 H); MS *m/z* M^+ 376 (90), $M^+ + 1$ (70), 361 (20), 319 (100). Anal. Calcd for $C_{23}H_{24}O_3Si$: C, 73.36; H, 6.42. Found: C, 73.06; H, 6.48.

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Registry No. **1**, 4394-76-7; **2**, 91-64-5; **3**, 82700-21-8; **4**, 134593-93-4; **5**, 134593-94-5; **6a**, 104210-91-5; **6b**, 86891-78-3; **6c**, 71096-87-2; **6d**, 130043-07-1; **6e**, 80738-05-2; **7a**, 134593-95-6; **7a′**, 134593-96-7; **7b**, 134678-35-6; **7c**, 134678-36-7; **8a-*cis***, 134593-97-8; **8a-*trans***, 134593-98-9; **8b-*cis***, 134678-37-8; **8b-*trans***, 134678-38-9; **8c**, 134678-39-0; **8d**, 134593-99-0; **9a**, 1846-76-0; **9b**, 21259-42-7; **10a**, 134627-02-4; **10b**, 134594-00-6; **11**, 66979-47-3; **12**, 134594-01-7; **13**, 23716-45-2; **14a**, 134594-02-8; **15a**, 134594-03-9; **15b**, 134594-04-0; **15e**, 134594-05-1; **16a**, 134594-06-2; **16b**, 134594-07-3; **16c**, 134627-03-5; **17b**, 134627-04-6; **17c**, 134594-08-4; **18a**, 134594-09-5; **18c**, 134594-10-8; **18d**, 134594-11-9; **19a**, 134594-12-0; **19b**, 134594-13-1; **19c**, 134678-40-3; **21**, 134594-14-2; **22**, 134594-15-3;

23, 130063-06-8; 24, 134594-16-4; 25, 130043-16-2; A, 119997-04-5; B, 134594-17-5; t-BuMe$_2$SiTf, 69739-34-0; PhCH=CHC(O)CH$_3$, 122-57-6; H$_3$CCOCH=C(CH$_3$)$_2$, 141-79-7; H$_2$C=CHCH$_2$Sn(Bu)$_3$, 24850-33-7; 1-acetylcyclopentene, 16112-10-0; 1-acetylcyclohexene, 932-66-1.

Supplementary Material Available: ^{1}H NMR spectra of compounds 7a', 7b, 7c, 8a-*cis*, 8a-*trans*, 8b-*cis*, 8b-*trans*, 8c, 8d, 10a, 10b, 14a, 15a, 16a–16c, 17b, 17c, 18a, 18c, 18d, 19a–19c, 21, 22, 23, 24, and 25 (33 pages). Ordering information is given on any current masthead page.

Lewis Acid Mediated Reaction of *N*-Phenyl-*S*-(4-methylphenyl)sulfoximidoyl Chloride with Alkenes

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The reaction of *N*-phenyl-*S*-(4-methylphenyl)sulfoximidoyl chloride (1) with alkenes in the presence of aluminum chloride leads to 2,1-benzothiazines in good yield. The reaction is regioselective, sometimes highly stereoselective, and is stereospecific with respect to alkene geometry. The mechanism can be formulated as a concerted cycloaddition between the iminosulfonium species 2 and the alkene to form a σ complex that subsequently rearomatizes to give the product.

The use of heterodiene cycloadditions in the construction of heterocyclic and carbocyclic organic compounds has been of considerable interest recently.[1] The facility with which these reactions are generally performed and their broad scope make them especially attractive in synthesis.[2] Heterodienes based on adjacent sulfur and nitrogen atoms are relatively rare and often not general with respect to reactivity. For example, *N*-sulfinylaniline has been used as the diene component in 4 + 2 cycloadditions, but only with reactive dienophiles.[3] Given the synthetic versatility associated with sulfur containing functional groups, it appeared that further study of this or related heterodiene systems was warranted. Herein we detail the results of such a study.

We recently reported the Lewis acid mediated reaction of *N*-phenyl-*S*-(4-methylphenyl)sulfoximidoyl chloride (1) with alkynes to produce benzothiazines 4 in good to high yield with high regioselectivity.[4,5] Although we initially believed the formation of the σ complex 3 to be stepwise, this process can, in principle, be formulated as a concerted cycloaddition between the iminosulfonium "heterodiene" 2 and the alkyne dienophile (Scheme I).[3,6] As part of our effort to explore the scope and mechanism of this process, we have examined alkenes as reactants and have found that the reaction is not only regioselective but sometimes highly stereoselective as well. Our results are shown in Table I.

Scheme I

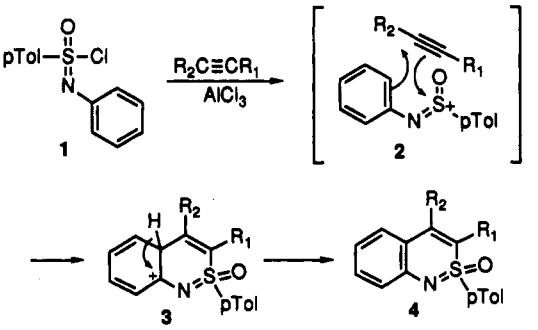
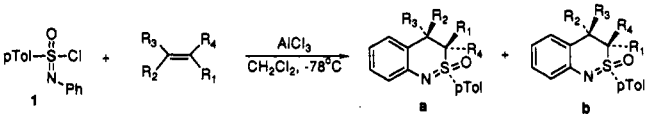


Table I. Reaction of 1 with Alkenes in the Presence of Lewis Acids



entry	R_1	R_2	R_3	R_4	products	yield[a] (%)	isomer ratio (a:b)
1	H	H	$-(CH_2)_4-$		5a/5b	91	25:1[c]
2	H	H	$-(CH_2)_3-$		6a/6b	81	5:1[b]
3	H	H	$-(CH_2)_5-$		7a/7b	70	2.4:1[b]
4	H	H	$-(CH_2)_6-$		8a/8b	76	2.1:1[b]
5	H	Et	H	Et	9a/9b	85	122:1[c]
6	H	H	Et	Et	10a/10b	85	2.3:1[c]
7	H	Bu	H	H	11a/11b	77	1.6:1[b]

[a] All yields are for chromatographically purified materials. [b] Isomer ratios were determined by HPLC analysis of crude reactions mixtures. [c] Isomer ratios were determined by weights of isolated products.

Entry 1 lists the intriguing result obtained with cyclohexene. Treatment of a mixture 1 and cyclohexene under either of our standard reaction conditions[4] gave a compound that was nearly a single isomer based on high-field ^{1}H and ^{13}C NMR and HPLC data. Two signals in the 300-MHz ^{1}H NMR of the major diastereomer 5a were

(1) For some recent examples and reviews, see: (a) Tietze, L. F. *J. Heterocycl. Chem.* **1990**, *27*, 47. (b) Tietze, L. F.; Fenner, J.; Anders, E. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1371. (c) Weinreb, S. M.; Scola, P. M. *Chem. Rev.* **1989**, *89*, 1525. (d) Taylor, E. C.; Macor, J. E. *J. Org. Chem.* **1989**, *54*, 1249, 4984. (e) Boger, D. L.; Kasper, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 1517. (f) Boger, D. L.; Robarge, K. D. *J. Org. Chem.* **1988**, *53*, 3373.

(2) Boger, D. L.; Weinreb, S. M. *Hetero Diels–Alder Methodology in Organic Synthesis*; Academic Press: San Diego, 1987.

(3) For examples and leading references, see: (a) Hanson, P.; Wren, S. A. C. *J. Chem. Soc., Perkin Trans. 2* **1987**, 197. (b) Borthakur, D. R.; Prajapati, D.; Sandhu, J. S. *Heterocycles* **1986**, *24*, 2739. (c) Zoller, U.; Roan, P. *Tetrahedron Lett.* **1985**, 2813. (d) Hanson, P.; Stone, T. W. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2429. (e) Hanson, P.; Lewis, R. J.; Stone, T. W. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1719. (f) Maculso, A.; Hamer, J. *J. Org. Chem.* **1067**, *32*, 506. (g) Collins, G. R. *Ibid.* **1964**, *29*, 1688.

(4) Harmata, M.; Schlemper, E. O. *Tetrahedron Lett.* **1987**, 5997.

(5) These benzothiazines are cyclic sulfoximines. For reviews of sulfoximine chemistry, see: (a) Johnson, C. R. *Aldrichimica Acta* **1985**, *18*, 3. (b) Johnson, C. R. in *Comprehensive Organic Chemistry*; Jones, N. D., Ed.; Pergamon: Oxford, 1979; Vol. 3, Chapter 11. (c) Kennewell, P. E.; Taylor, J. B. *Chem. Soc. Rev.* **1975**, 189.

(6) Many other cationic heterodienes are known. Among them are the cationic thiabutadienes that undergo facile 4 + 2 cycloaddition with alkenes. For examples, see: (a) Tamura, Y.; Ishiyawa, K.; Mizuki, Y.; Maeda, H.; Ishibashi, H. *Tetrahedron Lett.* **1981**, 3773. (b) Wada, M.; Shigehisa, T.; Kitani, H.; Akiba, K. *Ibid.* **1983**, 1715. (c) Thakur, D. K.; Vankar, Y. D. *Synthesis* **1983**, 223.

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