125761-96-8; (*R*)-**2b**, 102340-69-2; (*R*)-**2c**, 98639-89-5; (*R*)-**2d**, 102340-68-1; (*R*)-**2e**, 131933-99-8; (*S*)-**2f**, 125761-98-0; (*R*)-**2g**, 125761-99-1; (*R*)-**7a**, 130255-31-1; (*R*)-**7b**, 130323-19-2; (*R*)-**7c**, 130323-20-5; (*S*)-**7d**, 130255-33-3; (*S*)-**7e**, 130255-34-4; (*S*)-**7f**, 130255-35-5; (*S*)-**7g**, 130255-32-2; **8**, 109574-74-5; **9**, 123-72-8; **10**, 130323-25-0; **11**, 131934-00-4; (*S*)-**12**, 131934-01-5; (3*S*,4*S*)-**13**, 131973-33-6; (3*R*,4*S*)-**13**, 131934-04-8; (3*S*,4*S*)-**14**, 131934-02-6; (4*S*,5*S*)-**15**, 126910-76-7; (4*S*-*trans*)-**15**, 131934-03-7; ACHPA, 105192-90-3; CH_3CH_2CHO, 123-38-6; $CH_3(CH_2)_3CHO$, 110-62-3; $Me_2CHCH_2CH_2CHO$, 1119-16-0; $CyCH_2CH_2CHO$, 4361-28-8; $Me_2ThexSiO(CH_2)_3CHO$, 125382-48-1; Me_2CHCH_2CHO, 590-86-3; $PhCH_2CHO$, 122-78-1; CH_3CN, 75-05-8; $Me_2PhSiLi$, 3839-31-4; (1*S*,2*R*,5*S*)-menthyl (*R*)-(+)-4-chlorobenzenesulfinate, 109667-51-8; lipase, 9001-62-1.

Supplementary Material Available: ORTEP diagram and tables of crystallographic data collection, atomic coordinates, and anisotropic thermal parameters and ^1H and ^{13}C NMR spectra for each new compound described (32 pages). Ordering information is given on any current masthead page.

Tandem Reactions in 4-Siloxy-1-benzopyrylium Salts: Introduction of Substituents and Cyclohexene and Cyclopentane Annulation in Chromones

Yong-Gyun Lee, Kenji Ishimaru, Hideharu Iwasaki, Katsuo Ohkata, and Kin-ya Akiba*

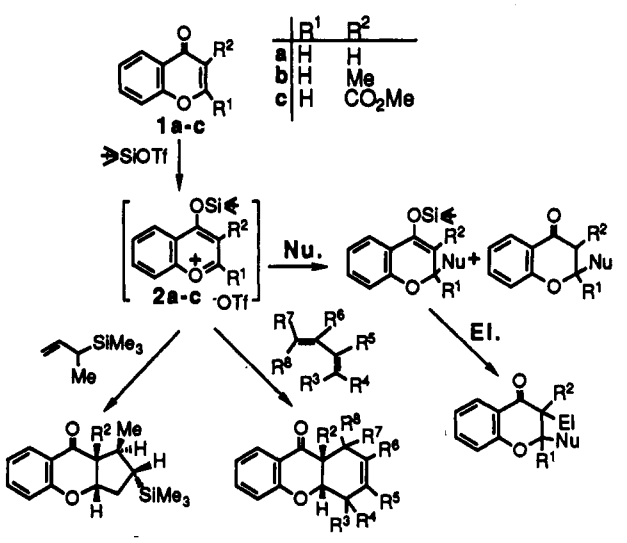
Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Naka-ku, Hiroshima 730, Japan

Received May 1, 1990

Reactions of 4-[(*tert*-butyldimethylsilyl)oxy]-1-benzopyrylium triflates (**2a–c**) with silyl enol ethers (**3a–d**) or allyl organometallic reagents (**5a–c**) afforded the corresponding 2-substituted 4-siloxy-2*H*-1-benzopyrans (**4a–d** and **6a–d**) along with 2,3-dihydrobenzopyrone derivatives (**7a–c**). An unexpected cyclopentane annulation to give **8a,b** was observed in the reaction of **2a,b** with 3-(trimethylsilyl)-1-butene (**5d**). Treatment of the products (**4a** and **6a**) with electrophiles (iminium salt, NBS, and NCS) converted them into the corresponding 2,3-disubstituted 2,3-dihydrobenzopyrone derivatives (**9a–c**). Reaction of benzopyrylium salts (**2a,b**) with α,β-unsaturated ketones (**10a–g**) in the presence of *tert*-butyldimethylsilyl triflate and 2,6-lutidine gave cyclohexene annulation products (xanthone derivatives, **11a–j**) in moderate to high yield. The reaction mechanisms are explained in terms of stereoelectronic and 1,3-allylic strain effects together with steric hindrance during the reaction.

Various natural products containing the chromone or xanthone skeletons have been isolated.[1] Introduction of substituents into chromone (4*H*-1-benzopyran-4-one) ring has been studied from the standpoint of the development of synthetic methodology and the mechanistic interest in the reactions of these heterocycles.[2] Although chromones can be regarded as α,β-unsaturated ketones, there are few synthetic methods for introduction of carbon nucleophiles at the C_2 position of the heterocyclic ring without ring opening or ring transformation of the heterocycle.[2a,e,f] In this connection, Wallace and his co-workers found that alkylcopper boron trifluoride complexes are effective in the introduction of an alkyl group into the C_2 position of chromone derivatives.[2g,i] Furthermore, they showed that cycloaddition of an activated chromone bearing an electron-withdrawing group at C_3 with butadienes gives xanthone derivatives by using a catalytic amount of titanium(IV) chloride.[3] However, this ring closure at the α,β-unsaturated ketone moiety of the chromone did not proceed without an activating group at C_3.

Scheme I



We have developed a facile and useful method for regioselective introduction of carbon nucleophiles into α-pyrones via pyrylium cations by means of *tert*-butyldimethylsilyl triflate.[4] During the course of this study, it

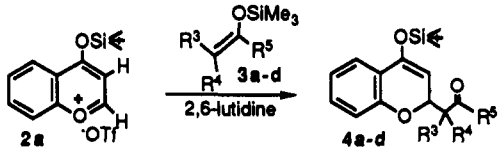
(1) (a) Dean, F. M. *Naturally Occurring Oxygen Ring Compounds*; Butterworths: London, 1963. (b) Ellis, G. P.; Lockhart, I. M. *Chromans and Tocopherols*; Wiley: New York, 1981. (c) Ellis, G. P. *Chromenes, Chromanones and Chromones*; Wiley: New York, 1977. (d) Nakagawa, A.; Omura, S.; Kushida, K.; Shimizu, H.; Lukacs, G. *J. Antibiot.* **1987**, *40*, 301. Omura, S.; Nakagawa, A.; Kushida, K.; Luckacs, G. *J. Am. Chem. Soc.* **1986**, *108*, 6088. (e) Kobayashi, K.; Nishimoto, C.; Ohya, J.; Sato, S.; Mikawa, T.; Shiobara, Y.; Kodama, M. *J. Antibiot.* **1988**, *41*, 741 and references therein.

(2) (a) Ellis, G. P. *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: New York, 1984; Vol. 3, Part 2b, p 647. (b) Hepworth, J. D. *Ibid.* p 737. (b) Cremins, P. J.; Wallace, T. W. *J. Chem. Soc., Chem. Commun.* **1984**, 1698. (c) Cremins, P. J.; Wallace, T. W. *Ibid.* **1986**, 1602. (d) Saengchantara, S. T.; Wallace, T. W. *J. Chem. Soc., Perkin Trans. 1* **1986**, 789. (e) Ghosh, C. K. *Heterocycl. Chem.* **1983**, *20*, 1437. (f) Chantegrel, B.; Nadi, A. I.; Gelin, S. *J. Org. Chem.* **1984**, *49*, 4419. (g) Wallace, T. W. *Tetrahedron Lett.* **1984**, *25*, 4299. (h) Clarke, P. D.; Fitton, A. O.; Suschitzky, H.; Wallace, T. W.; Dowlatshahi, H. A.; Suschitzky, J. L. *Ibid.* **1986**, *27*, 91. (i) Saengchantara, S. T.; Wallace, T. W. *J. Chem. Soc., Chem. Commun.* **1986**, 1592.

(3) Cremins, P. J.; Saengchantara, S. T.; Wallace, T. W. *Tetrahedron* **1987**, *43*, 3075.

0022-3263/91/1956-2058$02.50/0

Table I. Reactions of 2a with Silyl Enol Ethers and Ketene Silyl Acetal (3a–d)



entry	reactants		R³	R⁴	R⁵	product, yield (%)
1	2a	3a	H	H	OEt	4a, 96
2	2a	3b	H	H	i-Pr	4b, 95
3	2a	3c	H	Me	Et	4c, 96
4	2a	3d	H	H	C_6H_5	4d, 70

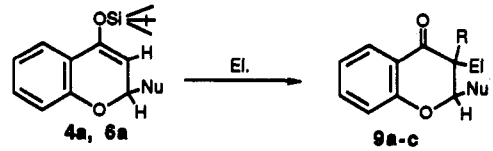
was observed that generation of siloxypyrylium salts was one of the most effective methods for activation of the pyrone ring in the absence of other activating groups. Moreover, a synthetic advantage of this method is the tandem introduction of two kinds of substituents successively at C_2 and C_3 in α-pyrones. These successful results prompted us to investigate reactions of chromones with various types of nucleophiles for preparation of 2-substituted chromone and xanthone derivatives. In this paper we report the introduction of substituents at the C_2 as well as the C_3 position and [3 + 2] and [4 + 2] annulations of the 4-siloxy-1-benzopyrylium salts as shown in Scheme I. We also wish to discuss some of the stereochemical details of these annulation reactions.[5]

Results and Discussion

Preparation of 4-[(*tert*-Butyldimethylsilyl)oxy]-1-benzopyrylium Salts (2). 4-Siloxy-1-benzopyrylium salts (**2a–c**) were prepared by heating chromones with an equimolar amount of *tert*-butyldimethylsilyl triflate without solvent (80 °C, ca. 1 h). For example, the formation of **2a** was confirmed by its ^1H NMR spectrum, indicating that the protons at the C_2 and C_3 positions of **2a** (δ 9.06 and 7.55) are shifted to lower field by more than 1 ppm relative to the corresponding protons of **1a** (δ 7.84 and 6.42 in $CDCl_3$ solution). The salts **2a–c** were dissolved in CH_2Cl_2 at room temperature and used without further purification for the following transformations due to easy decomposition under atmospheric moisture.

Tandem Reactions of 2 with a Nucleophile Followed by an Electrophile. Michael additions of silyl enol ethers and allyl organometallic reagents with α,β-unsaturated ketones are well documented.[6] We expected that 4-siloxy-1-benzopyrylium salts (**2**) would also react with these nucleophiles to furnish 2-substituted benzopyran derivatives. Reaction of **2a** derived from **1a** with ketene silyl acetal **3a** proceeded smoothly to give 2*H*-chromone **4a**, but treatment with **2a** with silyl enol ethers (**3b–d**) resulted in complex mixtures. By addition of 1 equiv of 2,6-lutidine to **3**, the reaction proceeded quite cleanly to afford the desired products (**4b–d**), which retained the silyl enol ether group almost quantitatively. These results are summarized in Table I.

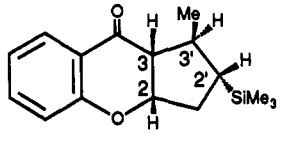
Scheme II



	Nu	R	El
9a	CH_2CO_2Et	CH_2=	
9b	CH_2CH=CH_2	H	Br
9c	CH_2CH=CH_2	H	Cl

Treatment of **2a** with allyltrimethylsilane (**5a**) in the presence of 2,6-lutidine afforded 2*H*-chromene **6a** in 22% yield along with the corresponding chromone (**7a**) in 12% yield. In the case of **2b**, only 2-allyl-2,3-dihydrochromone (**7b**) was obtained in 43% yield. As expected from the more strongly electron releasing effect of the stannyl group relative to the silyl group,[7] reaction of **2a** with allyltributylstannane (**5b**) under the same conditions gave the corresponding 4-siloxy-2*H*-chromene derivative (**6a**) in satisfactory yield. These results are summarized in Table II. Of particular note, reaction of **2d** with stannane **5b** gave the desired product (**6c**) in 15% yield, while the corresponding reaction with silane **5a** failed completely (entries 3 vs 6). Substitution at C_3 in the chromone ring by the methoxycarbonyl group not only produced the pyrylium salt (**2c**) under milder conditions (70 °C, 30 min), but also activated the siloxypyrylium ions for nucleophilic attack (entries 8, 9).

On the other hand, treatment of **2a** with 3-(trimethylsilyl)-1-butene (**5d**) did not give the expected allylation product such as **6e** but provided the unexpected five-membered ring derivative **8a** in 87% yield. In the reaction of **2b**, the corresponding cyclopentane annulation product (**8b**, 37%) was obtained along with allylation product (**6f**) as a minor product (9%). The stereochemistry of the five-membered ring in **8a** was determined on the basis of the vicinal coupling constants of $J_{2,3}$ and $J_{3,3'}$. The small coupling constant of $J_{2,3}$ (J = 3.7 Hz) indicates that the relative stereochemistry of the two methine protons is equatorial–axial or cis geometry. The $H_{3'}$ hydrogen is consistent with a trans relationship to the H_3 as judged from the relatively large coupling constants ($J_{3,3'}$ = 10.8 Hz). This assignment was supported by NOE experiments. An NOED spectrum showed an enhancement in the magnitude of the signal at δ 2.33 ($H_{2'}$, 8.7%) and δ 0.85 (Me, 4.7%), respectively, when the multiplet signal at δ 5.05 (H_2) was irradiated. Conversely, irradiation of the methyl group at δ 0.85 gave a 10% enhancement of the methine hydrogen at δ 5.05 (H_2). Although the relative stereochemistry of silyl and methyl groups could not be assigned from the vicinal coupling constant ($J_{2',3'}$ = 7.2 Hz), these NOE experiments indicate the trans geometry.



8a

Since the silyl enol ether function in the products remained intact after the above Michael type reactions, it was possible to introduce a second substituent into the

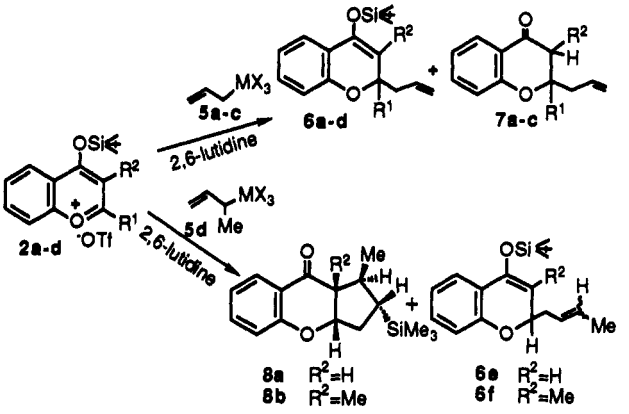
(4) Kume, T.; Kojima, T.; Iwasaki, H.; Yamamoto, Y.; Akiba, K.-y. *J. Org. Chem.* **1989**, *54*, 1931. Kume, T.; Akiba, K.-y. *Ibid.* **1989**, *54*, 1935.

(5) Preliminary reports: (a) Iwasaki, H.; Kume, T.; Yamamoto, Y.; Akiba, K.-y. *Tetrahedron Lett.* **1987**, *28*, 6355. (b) Lee, Y.-G.; Iwasaki, H.; Yamamoto, Y.; Ohkata, K.; Akiba, K.-y. *Heterocycles* **1989**, *29*, 35. (c) Ohkata, K.; Ishimaru, K.; Lee, Y.-G.; Akiba, K.-y. *Chem. Lett.* **1990**, 1725.

(6) (a) Narasaka, K.; Soai, K.; Aikawa, Y.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 779. (b) Saigo, K.; Osaki, M.; Mukaiyama, T. *Chem. Lett.* **1976**, 163. (c) Hosomi, A.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 1673. (d) Hosomi, A.; Hashimoto, H.; Kobayashi, H.; Sakurai, H. *Chem. Lett.* **1979**, 245.

(7) (a) Davis, D. D.; Gray, C. E. *J. Org. Chem.* **1970**, *35*, 1303. Davis, D. D.; Jacocks, H. M. III *J. Organomet. Chem.* **1981**, *206*, 33. (b) Traylor, T. G.; Koermer, G. S. *J. Org. Chem.* **1981**, *46*, 3651. (c) Lambert, J. B.; Wang, G.-t.; Teramura, D. H. *Ibid.* **1988**, *53*, 5422.

Table II. Allylation of 4-Siloxy-1-benzopyrylium Salts (2a–d) with Allyl Organometallic Reagents (5a–d)



entry	reactants				MX_3	products (6, 7, and 8) yield (%)[a]			
		R^1	R^2						
1	2a	H	H	5a	$SiMe_3$	6a	22 (33)	7a	12 (18)
2	2b	H	Me	5a	$SiMe_3$		0	7b	43 (64)
3	2d[b]	Me	H	5a	$SiMe_3$		0		0
4	2a	H	H	5b	$SnBu_3$	6a	85		0
5	2b	H	Me	5b	$SnBu_3$	6b	65		0
6	2d[b]	Me	H	5b	$SnBu_3$	6c	15		0
7	2a	H	H	5c	$SnPh_3$	6a	71		0
8	2c	H	CO_2Me	5a	$SiMe_3$	6d	30	7c	52
9	2c	H	CO_2Me	5b	$SnBu_3$	6d	75	7c	19
10	2a	H	H	5d	$SiMe_3$	6e	0	8a	87
11	2b	H	Me	5d	$SiMe_3$	6f	9	8b	37

[a] The yields in parentheses are based on recovered starting material. [b] The salt 2d is the 4-siloxy-1-benzopyrylium salt of the 2-methylchromone.

Table III. Cyclohexene Annulation of 2a,b with Siloxy Dienes 10a,g (See Scheme IIIa)

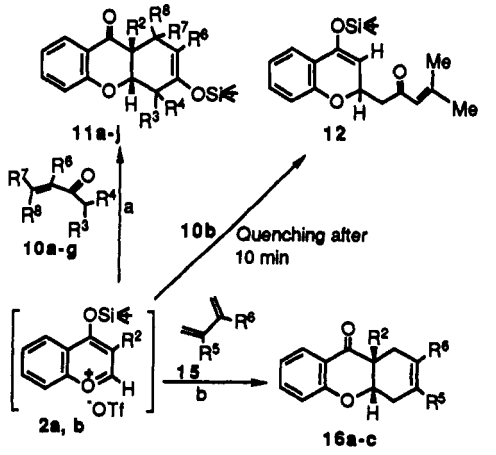
entry	reactants								reaction time (h)	products yield (%)	
		R^2		R^3	R^4	R^6	R^7	R^8			
1	2a	H	10a	H	H	H	H	H	3	11a	94
2	2a	H	10b	H	H	H	Me	Me	3	11b	92
3	2a	H	10c	H	H	H	Ph	H	2.5	11c	96
4	2a	H	10d	H	H		$-(CH_2)_3-$	H	4	11d	92
5	2a	H	10e	H	H		$-(CH_2)_4-$	H	2.5	11e	92
6	2a	H	10f	H	Me		$-(CH_2)_4-$	H	4	11f	85
7	2a	H	10g	H	Et		$-(CH_2)_4-$	H	6	11g	77
8	2b	Me	10c	H	H	H	Ph	H	10	11h	87
9	2b	Me	10f	H	Me		$-(CH_2)_4-$	H	4	11i	88
10	2b	Me	10g	H	Et		$-(CH_2)_4-$	H	10	11j	42

C_3-position of the 2-substituted 4-siloxy-2*H*-chromene. Reaction of **4a** with the appropriate iminium salt gave the 3-methylenebenzopyran-4-one derivative (**9a**) in 52% yield (Scheme II). Halogenation of **6a** with *N*-bromo- or *N*-chlorosuccinimide gave the 3-bromo- and 3-chloro-2,3-dihydrobenzopyrone (**9b** and **9c**) in 37% and 38% yields, respectively.

The ^1H NMR spectra of **9b** and **9c** show a small coupling constant (J = 1.8 Hz) between the H_2 and H_3. These results indicate that the two substituents may be arranged in a cis relationship where the allyl group is in the equatorial position and the incoming halogen group oriented axially (vide infra).

Cyclohexene Annulation Reactions of 2a,b. Cycloaddition of α,β-unsaturated carbonyl compounds promoted by means of Lewis acids has been extensively studied from synthetic and mechanistic viewpoints.[8] Though chromones contain an α,β-unsaturated ketone moiety, their use as 2π component in [4 + 2] cycloaddition reactions has received much less attention. In view of the successful tandem introduction of two types of substituents at C_2 and C_3 in the chromone ring via 4-siloxy-1-benzopyrylium salts (**2**) as described above, we undertook an exploration of the ability of the salts to participate in double Michael reac-

Scheme III. (See Table III and IV)



(8) (a) Fray, G. I.; Robinson, R. *J. Am. Chem. Soc.* **1961**, *83*, 249. (b) Inukai, T.; Kasai, M. *J. Org. Chem.* **1965**, *30*, 3567. (c) Harayama, T.; Cho, H.; Inubushi, Y. *Tetrahedron Lett.* **1975**, *31*, 2693. (d) Liu, H.-J.; Browne, E. N. C. *Can. J. Chem.* **1987**, *65*, 1262 and references therein.

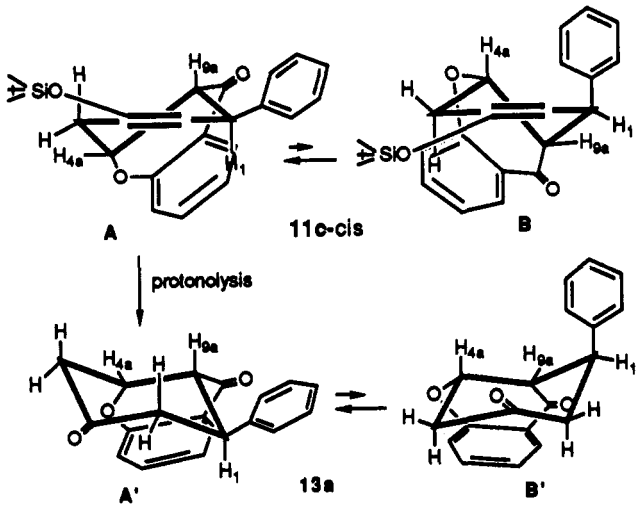


Figure 1.

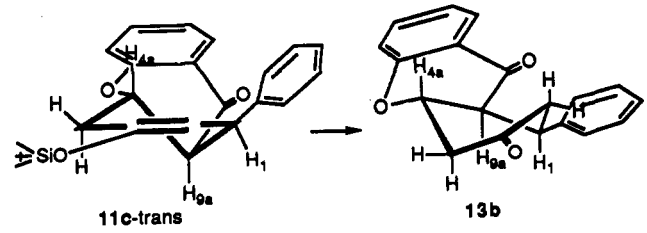


Figure 2.

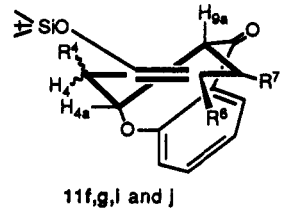


Figure 3.

tions or cyclohexene annulations.

Treatment of the pyrylium salts **2a,b** with α,β-unsaturated ketones (**10**) in the presence of 2 equiv of 2,6-lutidine and 1 equiv of *tert*-butyldimethylsilyl triflate (conditions for the in situ preparation of the silyl dienol ether) afforded the corresponding annulation products (**11**) in excellent yields as summarized in Table III and Scheme IIIa. When a sterically hindered α,β-unsaturated ketone such as **10g** was used as the diene equivalent, the products were obtained in moderate yields even after extended reaction time (entries 7, 10). Under the same reaction conditions, **2b** derived from 3-methylchromone, reacted with **10c,f** and **10g** to give the corresponding products (**11h–j**) (entries 8–10). Quenching of the reaction of **2a** with **10b** at an early stage afforded only a Michael type addition product (2-substituted 2*H*-chromene **12**) which underwent ring closure after longer reaction times. This result indicates that the present annulation reaction proceeds via a stepwise mechanism.

Structural assignments of the resulting annulation products were established from their ^{1}H NMR spectral data. For example, in the case of **11c**, the vinyl proton appears at δ 5.13 as a doublet (J = 5.0 Hz) and the signals due to the H_{4a} and H_{9a} are seen at δ 4.80 (ddd, J = 0.1, 3.1, and 6.4 Hz) and δ 2.90 (dd, J = 3.1 and 8.7 Hz), respectively. The small coupling constant (J = 3.1 Hz) between H_{4a} and H_{9a} indicates that the relative stereochemistry of the two methine protons is equatorial–axial.

The cyclohexene ring in **11c** is predicted to exist in two half-chair conformations as shown in Figure 1. The phenyl group at the C_1 position would prefer the pseudoequatorial position to the pseudoaxial, since a 1,3-diaxial interaction in the cyclohexene ring is considered to be more serious than an allylic 1,2-strain in the allylic part.[9] Therefore, conformer A would be favored over conformer B. Accordingly, the doublet of doublets at δ 2.90 may be assigned to the axial methine proton (H_{9a}) since it will be coupled to the adjacent equatorial proton (H_{4a}) by a small gauche coupling constant (J = 3.1 Hz) and the adjacent pseudoaxial proton (H_1) by a large anti coupling constant (J = 8.7 Hz). Protonolysis of **11c**-cis gave rise to the corresponding ketone **13a** in high yield. In its ^{1}H NMR spectrum, the methine proton (H_{9a}) appears as a doublet of doublets at δ 3.13 (J = 2.5 and 10.3 Hz). These spectral features also are consistent with the stereochemical assignment of **11c**-cis.

The cis product (**11c**-cis) was converted into a mixture of the geometric isomers (**11c**-trans/**11c**-cis = 2/1) by way of a series of reactions, that is, enolization with lithium diisopropylamide, trapping by chlorotrimethylsilane, and protonation with 10% aqueous hydrochloric acid at low temperature. Therefore, the initially formed cis derivative (**11c**-cis) must be the kinetically controlled product. The ^{1}H NMR spectrum of the **11c**-trans shows the vinyl proton at δ 4.85 as a doublet (J = 1.5 Hz), and the signals due to the H_{4a} and H_{9a} appear at δ 4.60 (ddd, J = 2.4, 9.2, and 13.3 Hz) and δ 3.10 (dd, J = 9.2, and 13.3 Hz), respectively.

The trans form (**11c**-trans), because of the nature of the ring fusion, is incapable of ring inversion.[10] According to analogous considerations to **11c**-cis, the most probable conformer of **11c**-trans is illustrated in Figure 2. The doublet of doublets at δ 3.10 (J = 9.2 and 13.3 Hz) can be assigned to the axial methine proton (H_{9a}), since it will be coupled to the adjacent axial proton (H_{4a}) by a large coupling constant (J = 13.3 Hz) and to the adjacent pseudo-equatorial proton by an unexpectedly large gauche coupling constant (J = 9.2 Hz). The extraordinary J value is attributable to distortion of the cyclohexene ring from the half-chair conformer due to a 1,3-diaxial interaction. The corresponding ketone **13b** which was obtained by protonolysis of **11c**-trans showed almost the same spectral features.

Since all of the other annulation products also show a small coupling constant (J = 2–3 Hz) between H_{4a} and H_{9a}, the ring junction is considered to have the same cis geometry as that of **11c**-cis.

On the other hand, the relative stereochemistry of the alkyl group at C_4 in **11f,g** and **11i,j** remains obscure from the intermediate magnitude of the vicinal coupling constant (J_{H4aH4} = 5–6 Hz) as shown in Figure 3. Although the relative stereochemistry of **11h–j** at C_1 could not be determined easily owing to the absence of a vicinal hydrogen at C_{9a}, the geometry of the ring junction (C_{4a}, C_{9a}) must be the same cis relationship as that of **11c**-cis according to the proposed reaction mechanism (vide infra). It is noteworthy that each of the above reactions gave rise to a single product among the four possible ones considering stereochemical options at C_{4a} and C_{9a}.

Reaction of **2d** derived from the 2-methylchromone under the same reaction conditions did not afford the

(9) (a) Allinger, N. L.; Nirsch, J. A.; Miller, M. A.; Tyminski, I. J. *J. Am. Chem. Soc.* **1968**, *90*, 5773. (b) Johnson, F.; Malhotra, S. K. *Ibid.* **1965**, *87*, 5492.

(10) Schubert, W.; Schafer, L.; Pauli, G. H. *J. Chem. Soc., Chem. Commun.* **1973**, 949.

Table IV. Cyclohexene Annulation of 2a,b with Dienes 15a,b (See Scheme IIIb)

entry	reactant					product, yield (%)[a]
		R^2		R^5	R^6	
1	2a	H	15a	H	Me	16a, 50 (74)
2	2a	H	15b	Me	Me	16b, 42 (100)
3	2b	Me	15b	Me	Me	16c, 25 (88)

[a] The yields in parentheses are based on recovered starting material.

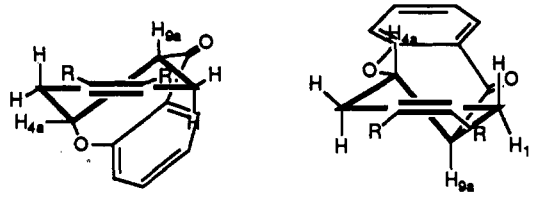
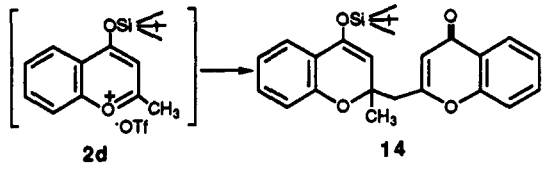


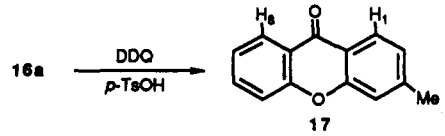
Figure 4.

desired annulation product; instead a dimerized product (14) was formed in quantitative yield, owing to the high acidity of the methyl protons.



Although 1a did not react with butadiene to give the corresponding cycloadduct in the absence of an activating group at C_3 such as the ethoxycarbonyl group,[3] reaction of 2a,b with an excess of isoprene (15a) or 2,3-dimethylbutadine (15b) produced the corresponding xanthone derivatives (16a–c) in moderate yields as shown in Table IV and Scheme IIIb. Structural assignment of the products (16a,b) was confirmed to be cis at C_{4a} and C_{9a} based on vicinal coupling constant (J_{H4aH9a} = 2.8 Hz) as shown in Figure 4. The trans derivative (16b') shows a relatively large coupling constant (J_{H4aH9a} = 13 Hz) as reported by Wallace et al.[3]

The regiochemistry of 16a was conclusively demonstrated by conversion to xanthone derivative 17, which was produced by dehydrogenation of 16a with DDQ in refluxing toluene in the presence of *p*-toluenesulfonic acid. The ^1H NMR spectrum of 17 displays the ortho proton (H_1) as a doublet (J = 8.1 Hz) at δ 8.23 and another ortho proton (H_8) as a doublet of doublets (J = 8.2, 1.7 Hz) at δ 8.34. These distinctly low field chemical shifts result from the "peri" deshielding effect by the carbonyl group. The structure of 17 is assigned to be 3-methylxanthone on the basis of the ^1H NMR spectral data. This high regioselectivity in the annulation of siloxypyrylium salt (2a) with isoprene can be explained by the known fact that increased polarization of the dienophilic double bond should lead to high para selectivity.[8d]



Mechanistic Considerations of Annulation Reaction. Although the stereochemistry in [4 + 2] type cycloadditions is easily understandable in terms of a concerted, one-step mechanism, the present [4 + 2] annulations probably proceed via a stepwise mechanism because

Scheme IV

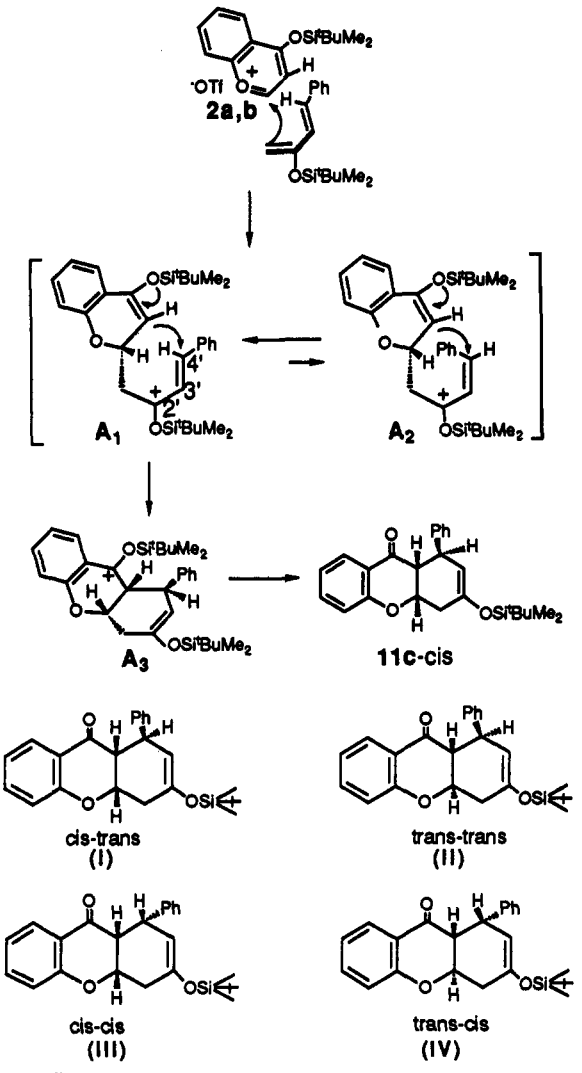


Figure 5.

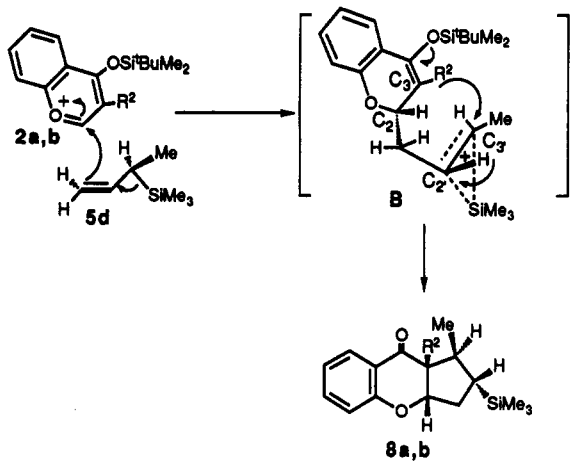
the conjugated siloxydienes are very polar reagents. Further, only Michael-type addition product 12 was obtained in the reaction between 2a and 10b after short reaction time (Scheme III). Therefore, it is necessary to explain reasonably the stereochemistry of reaction on the basis of the stepwise mechanism as shown in Scheme IV.

First, the siloxy diene derived from the α,β-unsaturated ketone (10c) under the reaction conditions attacks the siloxypyrylium salts (2a,b) at the C_2-position giving the intermediate siloxycarbinyl cation (A_1), which is stabilized by the neighboring siloxy and vinyl groups. The resulting silyl enolate of the 2*H*-chromene ring stereoselectively cyclizes onto the C_4-position to produce the more stable siloxycarbinyl cation (A_3), which is stabilized by the *o*-oxyphenyl and siloxy groups (Scheme IV).[11] Intermediate A_1 must be more stable than A_2 due to allylic 1,3-strain.[12] Furthermore, A_1 may react more smoothly to give a six-membered ring than A_2 because of the steric interaction during attack of the silyl enol ether in chromene ring on the allylic cation.

In other words, the highly stereoselective annulation reaction can be rationalized on the following basis. The silyl enol ether of the 2*H*-chromene ring can attack the

(11) Ohkata, K.; Mase, M.; Akiba, K.-y. *J. Chem. Soc., Chem. Commun.* 1987, 1727.
(12) (a) Johnson, F. *Chem. Rev.* 1968, *68*, 375. (b) Hoffmann, R. W. *Chem. Rev.* 1989, *89*, 1841.

Scheme V



conjugated siloxycarbinyl cation leading to four possible diastereomers (I–IV) in proportion to α- vs β-face attack and endo vs exo approach (Figure 5). From molecular models of annulation product **11c**, however, the transition state for endo approach leading to diastereomers III and IV is precluded because of the steric interaction between the 4-siloxy-2*H*-chromene moiety and the phenyl group attached to the allylic cation (A_2) in the stepwise reaction. In the transition states for exo approach, the silyl enol ether should be attacked from the pseudoaxial face by the siloxyallylcation owing to the stereoelectronic effect,[13] so that all of the reactions may proceed via a stepwise mechanism to give kinetically controlled cis fused diastereomer (I).

Finally, the mechanism we propose for the cyclopentane annulation is outlined in Scheme V. The allylic reagent (**5d**) attacks the siloxypyrylium salts (**2a,b**) at the C_2 position, giving the intermediate carbocation (B) which is stabilized by the trimethylsilyl and the methyl group. Attack by the emerging enolate at $C_{3'}$ forms the five-membered ring compound (**8a,b**). Generally, electrophiles attack allylic silanes anti to the silyl group.[14] Since there is undoubtedly interaction with the silicon in the transition state, the stereochemistry of the bridged intermediate (B) should be trans geometry due to stereoelectronic effect and allylic 1,3-strain.[12] Usually, carbocations such as B desilylate to produce olefins by the chloride ion generated from the Lewis acid in situ. In the reaction of **2a**, the favored pathway is cyclization. However, competition between cyclization and desilylation was observed in **2b** due to steric hindrance between the two methyl groups at the step of cyclization. According to these mechanistic considerations, the stereochemistry of **8b** must be the same as that of **8a**. This type of cyclization has been observed in reactions of allylstannanes with α,β-unsaturated acyliron complexes.[15] Allenylsilanes also undergo the analogous reaction with enones using Lewis acid catalysis,[16] but such a cyclopentane annulation of chromone derivatives is the first example to the best of our knowledge though cyclopropane, cyclobutane, and cyclohexane annulations have been reported.[3,17] The stereochemistry of ring junction (cis relationship) is also consistent with that expected from the proposed mechanism.

Experimental Section

Melting points were taken on a micro melting point apparatus and are uncorrected. Flash column chromatography was carried out on Merck silica gel 60, 230–400 mesh. Thin-layer chromatography (TLC) was performed with Merck silica gel GF-245 plates. Commercial vinyl bromide and allyltrimethylsilane were purchased from Kanto Chemicals and Aldrich Chemical Co. and distilled prior to use. Allylic stannane reagents[18] and *tert*-butyldimethylsilyl triflate[19] were prepared according to the literature, and α,β-unsaturated ketones were purchased or prepared by known methods.[20] Dichloromethane, chlorotrimethylsilane, and 2,6-lutidine were purified by distillation from CaH_2. Unless otherwise noted, material were obtained from commercial suppliers and were used without further purification. All reactions were conducted under a nitrogen atmosphere.

Preparation of 4-[(*tert*-Butyldimethylsilyl)oxy]-1-benzopyrylium Salts (2a–d). General Procedure. Into a two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum, and a gas inlet tube with a stopcock was placed chromone (**1a** or **1b**, 4.27 mmol). *tert*-Butyldimethylsilyl triflate (4.27 mmol) was added dropwise to the compound via syringe. After addition was complete, the mixture was stirred at 80 °C for 1 h without solvent. The resulting 4-siloxy-1-benzopyrylium salts (**2a,b**) were dissolved in CH_2Cl_2 at room temperature and used directly for reaction with silyl enol ethers (**3**), allyl organometallic reagents (**5**), α,β-unsaturated ketones (**10**), and dienes (**15**).

4-[(*tert*-Butyldimethylsilyl)oxy]-1-benzopyrylium trifluoromethanesulfonate (2a): ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 6 H), 0.90 (s, 9 H), 7.55 (d, J = 6.0 Hz, 1 H), 7.74–8.48 (m, 4 H), 9.06 (d, J = 6.0 Hz, 1 H).

4-[(*tert*-Butyldimethylsilyl)oxy]-3-methyl-1-benzopyrylium trifluoromethanesulfonate (2b): ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 6 H), 1.00 (s, 9 H), 2.10 (s, 3 H), 7.30–7.74 (m, 3 H), 8.05 (s, 1 H), 8.26 (dd, J = 7.0, 0.8 Hz, 1 H).

4-[(*tert*-Butyldimethylsilyl)oxy]-3-(methoxycarbonyl)-1-benzopyrylium trifluoromethanesulfonate (2c): ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 6 H), 1.10 (s, 9 H), 3.95 (s, 3 H), 7.35–7.85 (m, 3 H), 8.30 (dd, J = 7.1, 0.5 Hz, 1 H), 8.68 (s, 1 H).

4-[(*tert*-Butyldimethylsilyl)oxy]-2-methyl-1-benzopyrylium trifluoromethanesulfonate (2d): ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 6 H), 0.95 (s, 9 H), 2.84 (s, 3 H), 7.38 (s, 1 H), 7.64–8.17 (m, 3 H), 8.37 (dd, J = 8.6, 1.8 Hz, 1 H).

Reaction of 4-Siloxy-1-benzopyrylium Salt (2a) with Silyl Enol Ethers or Ketene Silyl Acetal (3) in the Presence of 2,6-Lutidine (Table I). General Procedure. To a solution of **2a** derived from **1a** (0.52 g, 3.56 mmol) in 10 mL of CH_2Cl_2 was added dropwise 2,6-lutidine (0.42 mL, 3.56 mmol) and silyl enol ether (**3b**, 0.85 g, 5.34 mmol) in 5 mL of CH_2Cl_2 at 0 °C. After the addition, the mixture was stirred at room temperature for ca. 1 h and then poured into ice-cooled 5% aqueous $NaHCO_3$ (50 mL) and 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 chromatography on silica gel using 20% ethyl acetate in hexane as eluent to afford 1.17 g (95%) of **4b** as a yellow oil.

(13) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Baldwin, J. E., Ed.; Pergamon Press: Oxford, England, 1983; Organic Chemistry Series Vol. 1, p 275.

(14) (a) Hayashi, T.; Kabeta, K.; Yamamoto, T.; Tamao, K.; Kumada, M. *Tetrahedron Lett.* **1983**, *24*, 5661. (b) Hayashi, T.; Konishi, M.; Ito, H.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4962.

(15) (a) Herndon, J. W. *J. Am. Chem. Soc.* **1987**, *109*, 3165. (b) Herndon, J. W.; Wu, C. *Tetrahedron Lett.* **1989**, *30*, 5745. (c) Herndon, J. W.; Wu, C. *Ibid.* **1989**, *30*, 6461.

(16) Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935.

(17) (a) Caplin, G. A.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc., Chem. Commun.* **1967**, 575; *J. Chem. Soc. C* **1968**, 2302. (b) Yamaoka, H.; Ohkata, K.; Hanafusa, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 245; Yamaoka, H. *J. Sci. Hiroshima Univ., Ser. A* **1980**, *44*, 171. (c) Dean, F. M.; Johnson, R. S. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2049. (d) Hanifin, J. W.; Cohen, E. *J. Am. Chem. Soc.* **1969**, *91*, 4494. (e) Elkaschef, M. A.-F.; Abdel-Megeid, F. M. E.; Mokhtar, K.-E.; Gad, F. A. *Acta Chem. Acad. Sci. Hung.* **1975**, *84*, 319.

(18) (a) Rosenberg, S. D.; Gibbons, A. I., Jr.; Ramsden, H. E. *J. Am. Chem. Soc.* **1957**, *79*, 2137. (b) Seyferth, D.; Weiner, M. A. *J. Org. Chem.* **1961**, *26*, 4797. (c) Binns, M. R.; Haynes, R. K.; Houston, T. L.; Jackson, W. R. *Tetrahedron Lett.* **1980**, *21*, 573.

(19) Corey, E. J.; Cho, H.; Rucker, C.; Hau, D. H. *Tetrahedron Lett.* **1981**, *22*, 3455.

(20) (a) Rand, L.; Dolinski, R. J. *J. Org. Chem.* **1966**, *31*, 3063. (b) Henne, A. L.; Tedder, J. M. *J. Chem. Soc.* **1953**, 3628.

4-[(*tert*-Butyldimethylsilyl)oxy]-2-[1-(ethoxycarbonyl)-1-methyl]-2*H*-1-benzopyran (4a): yellow oil, 0.65 g (96%); IR (neat, cm^{-1}) 2900, 1740, 1720, 1660, 1480, 1250; ^1H NMR ($CDCl_3$) δ 0.24 (s, 6 H), 1.03 (s, 9 H), 1.28 (t, J = 7.0 Hz, 3 H), 2.65 (dd, J = 15.0, 6.0 Hz, 1 H), 2.92 (dd, J = 15.0, 7.2 Hz, 1 H), 4.20 (q, J = 7.0 Hz, 2 H), 4.90 (d, J = 3.7 Hz, 1 H), 5.38 (ddd, J = 7.2, 6.0, 3.7 Hz, 1 H), 6.74–7.43 (m, 4 H); MS m/z M^+ 312 (35), 261 (40), 147 (100).

4-[(*tert*-Butyldimethylsilyl)oxy]-2-(3-methyl-2-oxobutyl)-2*H*-1-benzopyran (4b): yellow oil, 1.17 g (95%); IR (neat, cm^{-1}) 2950, 1700, 1650, 1460, 1020; ^1H NMR ($CDCl_3$) δ 0.25 (s, 6 H), 1.02 (s, 9 H), 1.05 (d, J = 1.2 Hz, 3 H), 1.15 (d, J = 1.2 Hz, 3 H), 2.49–2.53 (m, 1 H), 2.58 (dd, J = 19.0, 6.0 Hz, 1 H), 3.08 (dd, J = 19.0, 8.0 Hz, 1 H), 4.96 (d, J = 4.0 Hz, 1 H), 5.35 (ddd, J = 8.0, 6.0, 4.0 Hz, 1 H), 6.60–7.40 (m, 4 H); MS m/z M^+ 346 (35), 331 (48), 261 (100). Anal. Calcd for $C_{20}H_{30}O_3Si$: C, 69.32; H, 8.72. Found: C, 69.01; H, 8.69.

4-[(*tert*-Butyldimethylsilyl)oxy]-2-(1-methyl-2-oxobutyl)-2*H*-1-benzopyran (4c): yellow oil, 0.78 g (96%); IR (neat, cm^{-1}) 2900, 1710, 1640, 1460; ^1H NMR ($CDCl_3$) δ 0.19 (s, 3 H), 0.20 (s, 3 H), 0.98 (t, J = 7.1 Hz, 3 H), 1.00 (s, 9 H), 1.95 (d, J = 9.0 Hz, 3 H), 2.50 (q, J = 7.1 Hz, 2 H), 2.96 (dq, J = 9.6, 6.0 Hz, 1 H), 4.82 (d, J = 3.1 Hz, 1 H), 5.12 (dd, J = 6.0, 3.1 Hz, 1 H), 6.60–7.40 (m, 4 H); MS m/z M^+ 346 (15), 331 (28), 317 (8), 304 (15), 261 (100).

4-[(*tert*-Butyldimethylsilyl)oxy]-2-(2-oxo-2-phenylethyl)-2*H*-1-benzopyran (4d): yellow oil, 0.55 g (70%); ^1H NMR ($CDCl_3$) δ 0.28 (s, 6 H), 1.02 (s, 9 H), 3.22 (dd, J = 16.0, 4.0 Hz, 1 H), 3.58 (dd, J = 16.0, 8.0 Hz, 1 H), 5.05 (d, J = 4.0 Hz, 1 H), 5.50 (ddd, J = 8.0, 4.0, 0.4 Hz, 1 H), 6.70–8.08 (m, 9 H); MS m/z M^+ 380 (50), 261 (100), 248 (32).

Reaction of 2a–d with Allyl Organometallic Reagents (5a–d) (Table II). General Procedure Using Allyltrimethylsilane (5a). To a solution of **2a** derived from **1a** (0.56 g, 3.84 mmol) and 2,6-lutidine (0.45 mL, 3.84 mmol) in 7 mL of CH_2Cl_2 was added allyltrimethylsilane (0.95 mL, 5.76 mmol) in 2 mL of CH_2Cl_2 dropwise at 0 °C. After stirring for 4.5 h at room temperature, the solution was poured into ice-cooled 5% aqueous $NaHCO_3$ (50 mL). The mixture was extracted with CH_2Cl_2 (20 mL × 3), dried ($MgSO_4$), filtered, and evaporated to give a yellow oil. Purification by thin-layer chromatography using 20% ethyl acetate in hexane as eluent gave 0.255 g (22%) of **6a** and 0.086 g (12%) of **7a**, as a colorless oil, respectively.

General Procedure Using Allylstannane Reagents. To a solution of **2a** derived from **1a** (1.25 g, 8.56 mmol) in 10 mL of CH_2Cl_2 was added 2,6-lutidine (1.0 mL, 8.56 mmol), followed by allyltributylstannane (4.0 mL, 12.8 mmol) at 0 °C. The mixture was stirred for 3 h at room temperature, poured into ice-cooled 5% aqueous $NaHCO_3$ (150 mL), and extracted with CH_2Cl_2 (30 mL × 3). The combined CH_2Cl_2 solution was dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a yellow oil. Flash chromatography using 20% ethyl acetate in hexane as eluent gave 2.20 g (85%) of **6a** as a colorless oil.

4-[(*tert*-Butyldimethylsilyl)oxy]-2-(2-propenyl)-2*H*-1-benzopyran (6a): colorless oil, 2.20 g (85%); IR (neat, cm^{-1}) 2945, 1703, 1694, 1466, 1228; ^1H NMR ($CDCl_3$) δ 0.24 (s, 6 H), 1.05 (s, 9 H), 2.38–2.62 (m, 2 H), 4.79 (d, J = 3.5 Hz, 1 H), 4.92 (dd, J = 6.2, 3.5 Hz, 1 H), 5.00–5.30 (m, 2 H), 5.61–6.00 (m, 1 H), 6.60–6.90 (m, 2 H), 7.10 (dt, J = 7.7, 1.8 Hz, 1 H), 7.32 (dd, J = 7.5, 1.8 Hz, 1 H); MS m/z M^+ 302 (15), 287 (22), 261 (100); HRMS m/z calcd for $C_{18}H_{26}O_2Si$ 302.1700, found 302.1680.

4-[(*tert*-Butyldimethylsilyl)oxy]-3-methyl-2-(2-propenyl)-2*H*-1-benzopyran (6b): colorless oil, 1.05 g (65%); IR (neat, cm^{-1}) 2940, 1690, 1510, 1465, 1230; ^1H NMR ($CDCl_3$) δ 0.05 (s, 3 H), 0.10 (s, 3 H), 0.99 (s, 9 H), 1.66 (s, 3 H), 2.33–2.50 (m, 2 H), 4.68 (dd, J = 7.7, 4.4 Hz, 1 H), 4.90–5.15 (m, 2 H), 5.60–6.12 (m, 1 H), 6.60–7.30 (m, 4 H); MS m/z M^+ 316 (15), 301 (25), 275 (100).

4-[(*tert*-Butyldimethylsilyl)oxy]-2-methyl-2-(2-propenyl)-2*H*-1-benzopyran (6c): colorless oil, 0.23 g (15%); ^1H NMR ($CDCl_3$) δ 0.05 (s, 3 H), 0.10 (s, 3 H), 0.90 (s, 9 H), 1.04 (s, 3 H), 2.30–2.52 (m, 2 H), 4.76 (s, 1 H), 5.15–5.95 (m, 2 H), 5.70–6.10 (m, 1 H), 6.70–7.40 (m, 4 H); MS m/z M^+ 316 (18), 300 (30), 276 (100).

4-[(*tert*-Butyldimethylsilyl)oxy]-3-(methoxycarbonyl)-2-(2-propenyl)-2*H*-1-benzopyran (6d): colorless oil, 0.48 g (75%); ^1H NMR ($CDCl_3$) δ 0.10 (s, 3 H), 0.26 (s, 3 H), 1.17 (s, 9 H), 2.20–2.70 (m, 2 H), 3.75 (s, 3 H), 4.80–5.08 (m, 2 H), 5.32 (dd, J = 8.6, 4.6 Hz, 1 H), 5.60–6.10 (m, 1 H), 6.80–7.50 (m, 4 H); MS m/z M^+ 360 (15), 345 (20), 329 (15), 319 (100); HRMS m/z calcd for $C_{20}H_{28}O_4Si$ 360.1832, found 360.1795.

2,3-Dihydro-2-(2-propenyl)-4*H*-1-benzopyran-4-one (7a): colorless oil, 0.086 g (12%); ^1H NMR ($CDCl_3$) δ 2.48–2.95 (m, 4 H), 4.45–4.70 (m, 1 H), 5.08–5.35 (m, 2 H), 5.88 (ddt, J = 17.7, 9.6, 6.8 Hz, 1 H), 6.90–7.02 (m, 2 H), 7.42 (ddd, J = 8.5, 7.0, 1.9 Hz, 1 H), 7.84 (dd, J = 8.2, 1.9 Hz, 1 H); MS m/z M^+ 188 (85), M^+ + 1 (21), 147 (100); HRMS m/z calcd for $C_{12}H_{12}O_2$ 188.0836, found 188.0823.

2,3-Dihydro-3-methyl-2-(2-propenyl)-4*H*-1-benzopyran-4-one (7b): colorless oil, 0.47 g (43%); ^1H NMR ($CDCl_3$) δ 1.15 (d, J = 7.3 Hz, 3 H), 2.35–2.97 (m, 3 H), 4.55 (ddd, J = 7.9, 6.4, 2.9 Hz, 1 H), 5.15–5.40 (m, 2 H), 5.96 (dddd, J = 17.6, 7.9, 7.5, 6.2 Hz, 1 H), 6.95–7.00 (m, 2 H), 7.42 (ddd, J = 8.5, 7.0, 1.9 Hz, 1 H), 7.84 (dd, J = 8.2, 1.9 Hz, 1 H); MS m/z M^+ 202 (100), M^+ + 1 (50), 160 (80).

2,3-Dihydro-3-(methoxycarbonyl)-2-(2-propenyl)-4*H*-1-benzopyran-4-one (7c): colorless oil, 0.18 g (19%): ^1H NMR ($CDCl_3$) δ 2.25–2.80 (m, 2 H), 3.65 (d, J = 2.5 Hz, 1 H), 3.75 (s, 3 H), 4.68–5.00 (m, 1 H), 5.10–5.30 (m, 2 H), 5.60–6.00 (m, 1 H), 6.80–7.90 (m, 4 H); MS m/z M^+ 246 (100), M^+ + 1 (25), 205 (85).

Reaction of 2a,b with 3-(Trimethylsilyl)-1-butene (5d).[21] General procedure was the same as the reaction of **2a** with allyl trimethylsilane (**5d**).

1,2,3,3a,9,9a-Hexahydro-1-methyl-2-(trimethylsilyl)cyclopenta[*b*][1]benzopyran-9-one (8a): colorless oil, 1.57 g (87%); IR (neat, cm^{-1}) 2955, 1607, 1473, 1351, 1123, 1026; ^1H NMR ($CDCl_3$) δ 0.03 (s, 9 H), 0.85 (d, J = 7.1 Hz, 3 H), 1.27 (ddd, J = 12.9, 7.2, 7.2 Hz, 1 H), 1.67 (ddd, J = 12.9, 12.9, 3.7 Hz, 1 H), 2.33 (dd, J = 12.9, 7.2 Hz, 1 H), 2.54 (ddq, J = 10.8, 7.2, 7.2 Hz, 1 H), 2.77 (dd, J = 10.8, 3.7 Hz, 1 H), 5.05 (dd, J = 3.7, 3.7 Hz, 1 H), 6.80–7.00 (m, 2 H), 7.42 (ddd, J = 8.5, 7.0, 1.9 Hz, 1 H), 7.84 (dd, J = 8.3, 1.9 Hz, 1 H); MS m/z M^+ 274 (100), M^+ + 1 (25), M^+ + 2 (8.7), 259 (23), 220 (81), 218 (75). Anal. Calcd for $C_{16}H_{22}O_2Si$: C, 70.03; H, 8.08. Found: C, 69.99; H, 8.32.

1,2,3,3a,9,9a-Hexahydro-1,9a-dimethyl-2-(trimethylsilyl)cyclopenta[*b*][1]benzopyran-9-one (8b): colorless oil, 0.36 g (29%); ^1H NMR ($CDCl_3$) δ 0.08 (s, 9 H), 0.96 (d, J = 7.1 Hz, 3 H), 1.23 (s, 3 H), 1.30 (ddd, J = 12.9, 8.9, 8.9 Hz, 1 H), 1.90 (ddd, J = 14.0, 12.9, 3.3 Hz, 1 H), 1.94 (dd, J = 8.2, 7.1 Hz, 1 H), 2.23 (dd, J = 14.0, 8.2 Hz, 1 H), 4.56 (d, J = 3.3 Hz, 1 H), 6.81–7.01 (m, 2 H), 7.42 (ddd, J = 8.5, 7.0, 1.9 Hz, 1 H), 7.84 (dd, J = 8.3, 1.9 Hz, 1 H); MS m/z M^+ 288 (100), M^+ + 1 (32), M^+ + 2 (12), 273 (28), 215 (30).

4-[(*tert*-Butyldimethylsilyl)oxy]-2-(2-butenyl)-3-methyl-2*H*-1-benzopyran (6f): colorless oil, 0.15 g (9%); IR (neat, cm^{-1}) 2930, 1632, 1470, 1228; ^1H NMR ($CDCl_3$) δ 0.16 (s, 3 H), 0.23 (s, 3 H), 1.10 (s, 9 H), 1.79 (s, 3 H), 1.84 (s, 3 H), 2.25–2.72 (m, 2 H), 4.60–4.82 (m, 1 H), 5.45–5.70 (m, 2 H), 6.70–7.35 (m, 4 H). MS m/z 330 (M^+); HRMS m/z calcd for $C_{20}H_{30}O_2Si$ 330.2016, found 330.2028.

Reaction of 4a with an Iminium Salt. To a suspension of 5.13 mmol of *N,N*-diethyl-*N*-methyleneammonium chloride[22] in 5 mL of CH_2Cl_2 was added 1.50 g (4.80 mmol) of **4a** in 3 mL of CH_2Cl_2 at room temperature. The reaction mixture was stirred for 5 h and then poured into 30 mL of ice-cooled 5% aqueous Na_2CO_3, and the mixture was extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$), filtered, and evaporated to give a yellow oil. Purification by thin-layer chromatography using 20% ethyl acetate in hexane as eluent gave 0.62 g (52%) of **9a** as a pale yellow oil: IR (neat, cm^{-1}) 1750, 1700, 1540, 1480, 1130; ^1H NMR ($CDCl_3$) δ 1.25 (t, J = 7.3 Hz, 3 H), 2.77 (dd, J = 15.4, 6.2 Hz, 1 H), 2.99 (dd, J = 15.4, 7.4 Hz, 1 H), 4.20 (q, J = 7.3 Hz, 2 H), 5.47 (dd, J = 7.4, 1.5 Hz, 1 H), 5.56 (d, J = 0.8 Hz, 1 H), 6.36 (dd, J = 0.8 Hz, 1 H), 6.88–7.11 (m, 2 H), 7.38–7.57 (m, 1 H), 7.90–8.00 (m, 1 H); MS m/z M^+ 246 (80), 174 (100), 201 (50); HRMS m/z calcd for $C_{14}H_{14}O_4$ 246.0891, found 246.0873.

Reaction of 6a with *N*-Bromo- or *N*-Chlorosuccinimide (NBS or NCS). General Procedure. To a solution of **6a** (0.86

(21) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678.
(22) Rochin, C.; Babot, O.; Dunogues, J.; Duboudin, F. *Synthesis* **1986**, 228.

g, 2.84 mmol) in 5 mL of CH_2Cl_2 at 0 °C was added dropwise a solution of *N*-bromosuccinimide (0.53 g, 3.0 mmol) in 5 mL of CH_2Cl_2. After addition was complete, the reaction mixture was warmed to room temperature and poured into ice-cooled water (30 mL). The mixture was extracted with CH_2Cl_2 (3 × 20 mL), and the organic layers were combined, washed with water (2 × 30 mL), and dried ($MgSO_4$). The solvent was removed in vacuo, and the residue was separated by thin-layer chromatography (hexane–ethyl acetate = 5:1 as an eluent) to afford 0.28 g (37%) of **9b** as a yellow oil.

3-Bromo-2,3-dihydro-2-(2-propenyl)-4*H*-1-benzopyran-4-one (9b): yellow oil, 0.28 g (37%); IR (neat, cm^{-1}) 2950, 1710, 1615, 1460, 1320, 1110; ^1H NMR ($CDCl_3$) δ 2.40–3.00 (m, 2 H), 4.21 (ddd, *J* = 7.5, 6.6, 1.8 Hz, 1 H), 4.56 (d, *J* = 1.8 Hz, 1 H), 5.05–5.40 (m, 2 H), 5.90 (dddd, *J* = 17.4, 7.9, 7.9, 5.9 Hz, 1 H), 6.83–7.02 (m, 2 H), 7.42 (ddd, *J* = 8.5, 7.0, 1.9 Hz, 1 H), 7.84 (dd, *J* = 8.2, 1.9 Hz, 1 H); MS *m/z* M^+ 266 (100), M^+ + 1 (20), M^+ + 2 (85), 227 (90), 189 (12), 187 (95); HRMS *m/z* calcd for $C_{12}H_{11}O_2{}^{79}Br$ 265.9942, found 265.9939; calcd for $C_{12}H_{11}O_2{}^{81}Br$ 267.9921, found 267.9906.

3-Chloro-2,3-dihydro-2-(2-propenyl)-4*H*-1-benzopyran-4-one (9c): yellow oil, 0.20 g (38%); IR (neat, cm^{-1}) 2950, 1715, 1620, 1460, 1320, 1025; ^1H NMR ($CDCl_3$) δ 2.40–2.90 (m, 2 H), 4.28 (d, *J* = 1.8 Hz, 1 H), 4.45 (m, 1 H), 5.10–5.38 (m, 2 H), 5.50–6.00 (m, 1 H), 6.80–7.00 (m, 2 H), 7.42 (ddd, *J* = 8.5, 7.0, 1.9 Hz, 1 H), 7.84 (dd, *J* = 8.2, 1.9 Hz, 1 H); MS *m/z* M^+ 222 (100), M^+ + 1 (50), M^+ + 2 (80), 187 (15), 185 (75). HRMS *m/z* calcd for $C_{12}H_{11}O_2{}^{35}Cl$ 222.0447, found 222.0462; calcd for $C_{12}H_{11}O_2{}^{37}Cl$ 224.0417, found 224.0382.

Reaction of 2a,b with α,β-Unsaturated Ketones (10a–g) in the Presence of *tert*-Butyldimethylsilyl Triflate and 2,6-Lutidine (Table III). General Procedure. To a solution of **2a** derived from **1a** (0.67 g, 4.59 mmol) and 2,6-lutidine (0.55 mL, 9.18 mmol) in 5 mL of CH_2Cl_2 at room temperature was added *tert*-butyldimethylsilyl triflate (1.0 mL, 4.59 mmol) and benzalacetone (0.67 g, 4.59 mmol) in 5 mL of CH_2Cl_2, and the mixture was refluxed for 2.5 h. After cooling, the mixture was poured into ice-cooled 5% $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2 (30 mL × 3), and the combined organic layers were dried ($MgSO_4$). The solvent was removed in vacuo, and the residue was purified by flash chromatography on silica gel using 10% ethyl acetate in hexane as eluent gave 1.79 g (96%) of **11c-cis** as a yellow oil.

3-[(*tert*-Butyldimethylsilyl)oxy]-1,4,4a,9a-tetrahydro-9*H*-xanthen-9-one (11a): yellow oil, 0.55 g (94%); IR (neat, cm^{-1}) 2960, 1690, 1600, 1420, 1220; ^1H NMR ($CDCl_3$) δ 0.20 (s, 6 H), 0.96 (s, 9 H), 2.20–2.63 (m, 4 H), 2.76 (ddd, *J* = 10.3, 6.9, 2.6 Hz, 1 H), 4.82 (ddd, *J* = 2.6, 2.4, 1.7 Hz, 1 H), 4.88–5.03 (m, 1 H), 6.90–7.93 (m, 4 H). MS *m/z* M^+ 330 (100), M^+ + 1 (30), M^+ + 2 (11), 311 (25), 273 (90). This compound **11a** is readily desilylated under atmospheric moisture to give the corresponding ketone (semisolid): ^1H NMR ($CDCl_3$) δ 2.05–3.10 (m, 7 H), 4.97 (m, 1 H), 6.95–8.00 (m, 4 H); HRMS *m/z* calcd for $C_{13}H_{12}O_3$ 216.0785, found 216.0769.

3-[(*tert*-Butyldimethylsilyl)oxy]-1,4,4a,9a-tetrahydro-9a-methyl-9*H*-xanthen-9-one (11b): yellow oil, 0.62 g (92%); IR (neat, cm^{-1}) 2900, 1690, 1600, 1460, 1220; ^1H NMR ($CDCl_3$) δ 0.15 (s, 3 H), 0.18 (s, 3 H), 0.92 (s, 3 H), 0.95 (s, 9 H), 1.18 (s, 3 H), 2.35 (d, *J* = 2.9 Hz, 1 H), 2.52 (dd, *J* = 4.0, 1.8 Hz, 1 H), 2.56 (dd, *J* = 4.0, 0.9 Hz, 1 H), 4.74 (ddd, *J* = 2.9, 1.8, 0.9 Hz, 1 H), 4.78 (s, 1 H), 6.88–7.99 (m, 4 H). MS *m/z* M^+ 358 (70), M^+ + 1 (20), M^+ + 2 (6), 343 (53), 301 (30), 295 (100); HRMS *m/z* calcd for $C_{21}H_{30}O_3Si$ 358.1962, found 358.1961.

3-[(*tert*-Butyldimethylsilyl)oxy]-1,4,4a,9a-tetrahydro-1-phenyl-9*H*-xanthen-9-one (11c-cis): yellow oil, 1.79 g (96%); IR (neat, cm^{-1}) 2980, 1680, 1600, 1460, 1220; ^1H NMR ($CDCl_3$) δ 0.24 (s, 3 H), 0.27 (s, 3 H), 0.98 (s, 9 H), 2.66 (dd, *J* = 6.4, 1.0 Hz, 1 H), 2.68 (dd, *J* = 1.0, 0.1 Hz, 1 H), 2.90 (dd, *J* = 8.7, 3.1 Hz, 1 H), 3.95 (dd, *J* = 8.7, 5.0 Hz, 1 H), 4.80 (ddd, *J* = 6.4, 3.1, 0.1 Hz, 1 H), 5.13 (d, *J* = 5.0 Hz, 1 H), 6.53–7.52 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ −4.19, −4.11, 18.1, 25.7, 34.4, 41.1, 47.9, 75.6, 105.7, 117.3, 120.6, 121.2, 126.4, 126.7, 127.2, 129.9, 135.1, 139.3, 148.1, 160.9, 194.6; MS *mz* M^+ 406 (100), M^+ + 1 (34), M^+ + 2 (14), 391 (10), 363 (28); HRMS *m/z* calcd for $C_{25}H_{30}O_3Si$ 406.1962, found 406.1956.

Isomerization of 11c-cis with LDA. To a suspension of lithium diisopropylamide (LDA) solution (2.19 mmol) in 7 mL of dry THF was added 0.86 g (2.19 mmol) of **11c-cis** in 3 mL of THF at −78 °C. After stirring for 30 min at −78 °C, chlorotrimethylsilane (0.28 mL, 2.19 mmol) was added dropwise. After 30 min, the mixture was quenched with 10% HCl (30 mL) and the solution was stirred for 40 min at room temperature. The resulting aqueous residue was diluted with 50 mL of CH_2Cl_2 and washed sequentially with water (30 mL × 2). The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by TLC using 40% ethyl acetate in hexane to give 0.15 g (16.8%) of 11-cis and 0.37 g (41.6%) of **11c-trans**. **11c-trans**: yellow oil; ^1H NMR ($CDCl_3$) δ 0.25 (s, 6 H), 0.96 (s, 9 H), 2.75–2.95 (m, 2 H), 3.10 (dd, *J* = 13.3, 9.2 Hz, 1 H), 4.02 (dd, *J* = 9.2, 1.5 Hz, 1 H), 4.60 (ddd, *J* = 13.3, 9.2, 2.4 Hz, 1 H), 4.85 (d, *J* = 1.5 Hz, 1 H), 6.95–7.85 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ −4.48, −4.30, 17.9, 25.6, 36.0, 39.9, 52.5, 76.9, 108.3, 117.2, 121.0, 121.2, 126.2, 127.0, 128.2, 128.3, 128.5, 135.5, 145.3, 160.5, 192.9; MS *m/z* M^+ 406; HRMS *m/z* calcd for $C_{25}H_{30}O_3Si$ 406.1962, found 406.1952.

4-[(*tert*-Butyldimethylsilyl)oxy]-1,2,3,5,5a,11,11a,11b-octahydrobenz[*b*]indeno[4,5-*e*]pyran-11-one (11d): yellow oil, 0.87 g (92%); IR (neat, cm^{-1}) 2950, 1700, 1610, 1480, 1300; ^1H NMR ($CDCl_3$) δ 0.15 (s, 6 H), 0.95 (s, 9 H), 1.60–2.94 (m, 9 H), 3.15 (dd, *J* = 6.5, 4.4 Hz, 1 H), 4.92 (ddd, *J* = 6.5, 6.5, 4.4 Hz, 1 H), 6.84–7.88 (m, 4 H); MS *m/z* M^+ 370 (100), 315 (35), 224 (80). This compound **11d** is readily desilylated under atmospheric moisture to give the corresponding ketone (semisolid): ^1H NMR ($CDCl_3$) δ 1.20–3.00 (m, 10 H), 3.20 (dd, *J* = 6.5, 3.3 Hz, 1 H), 4.97 (m, 1 H), 6.90–8.00 (m, 4 H); HRMS *m/z* calcd for $C_{16}H_{16}O_3$ 256.1099, found 256.1084.

5-[(*tert*-Butyldimethylsilyl)oxy]-1,2,3,4,6,6a,12a,12b-octahydro-12*H*-benzo[*a*]xanthen-12-one (11e): colorless crystalline solid, 1.24 g (92%); mp 110–112 °C; ^1H NMR ($CDCl_3$) δ 0.18 (s, 6 H), 0.98 (s, 9 H), 1.05–1.79 (m, 8 H), 2.54–2.62 (bs, 2 H), 2.75 (dd, *J* = 8.2, 2.9 Hz, 1 H), 2.97 (dd, *J* = 11.9, 1.3 Hz, 1 H), 4.72 (ddd, *J* = 2.9, 2.3, 1.3 Hz, 1 H), 6.90–7.96 (m, 4 H); MS *m/z* M^+ 384 (100), M^+ + 1 (33), M + 2 (12), 369 (4.5), 327 (25); HRMS *m/z* calcd for $C_{23}H_{32}O_3Si$ 384.2119, found 384.2117. Anal. Calcd for $C_{23}H_{32}O_3Si$: C, 71.83; H, 8.39. Found: C, 71.59; H, 8.01.

5-[(*tert*-Butyldimethylsilyl)oxy]-1,2,3,4,6,6a,12a,12b-octahydro-6-methyl-12*H*-benzo[*a*]xanthen-12-one (11f): colorless crystalline solid, 0.92 g (85%); mp 145–146 °C; ^1H NMR ($CDCl_3$) δ 0.12 (s, 3 H), 0.15 (s, 3 H), 0.97 (s, 9 H), 1.23–1.42 (m, 7 H), 1.58 (s, 3 H), 2.42–2.65 (bm, 2 H), 2.75 (dd, *J* = 8.4, 2.4 Hz, 1 H), 2.90 (bs, 1 H), 4.50 (dd, *J* = 5.8, 2.4 Hz, 1 H), 6.87–7.92 (m, 4 H); MS *m/z* M^+ 398 (100), M^+ + 1 (33), M^+ + 2 (20), 341 (25), 323 (11.6). Anal. Calcd for $C_{24}H_{34}O_3Si$: C, 72.31; H, 8.60. Found: C, 72.11; H, 8.83.

5-[(*tert*-Butyldimethylsilyl)oxy]-6-ethyl-1,2,3,4,6,6a,-12a,12b-octahydro-12*H*-benzo[*a*]xanthen-12-one (11g): colorless crystalline solid, 0.88 g (77%); mp 147–149 °C; ^1H NMR ($CDCl_3$) δ 0.12 (s, 3 H), 0.16 (s, 3 H), 0.96 (t, *J* = 7.2 Hz, 3 H), 1.00 (s, 9 H), 1.20–1.82 (m, 7 H), 2.00 (m, 2 H), 2.23–2.50 (bm, 2 H), 2.75 (dd, *J* = 7.9, 2.4 Hz, 1 H), 2.90 (bs, 1 H), 4.67 (dd, *J* = 5.5, 2.4 Hz, 1 H), 6.90–7.94 (m, 4 H); MS *m/z* M^+ 412 (100), M^+ + 1 (33), M^+ + 2 (13), 355 (30), 226 (91). Anal. Calcd for $C_{25}H_{36}O_3Si$: C, 72.77; H, 8.78. Found: C, 72.71; H, 8.79.

3-[(*tert*-Butyldimethylsilyl)oxy]-1,4,4a,9a-tetrahydro-9a-methyl-1-phenyl-9*H*-xanthen-9-one (11h): yellow oil, 1.25 g (87%); ^1H NMR ($CDCl_3$) δ 0.25 (s, 3 H), 0.28 (s, 3 H), 1.03 (s, 9 H), 1.50 (s, 3 H), 2.65 (m, 2 H), 3.50 (d, *J* = 4.8 Hz, 1 H), 4.46 (dd, *J* = 3.5, 0.9 Hz, 1 H), 5.10 (d, *J* = 4.8 Hz, 1 H), 6.75–7.52 (m, 9 H); MS *m/z* M^+ 420 (100), M^+ + 1 (40), M^+ + 2 (13), 405 (23), 363 (25).

5-[(*tert*-Butyldimethylsilyl)oxy]-1,2,3,4,6,6a,12a,12b-octahydro-6,9a-dimethyl-12*H*-benzo[*a*]xanthen-12-one (11i): colorless crystalline solid, 0.98 g, (88%); mp 132–134 °C; ^1H NMR ($CDCl_3$) δ 0.05 (s, 3 H), 0.10 (s, 3 H), 0.93 (s, 9 H), 1.20 (s, 3 H), 1.25–1.35 (m, 8 H), 1.59 (s, 3 H), 2.50–2.81 (m, 2 H), 4.08 (d, *J* = 5.2 Hz, 1 H), 6.87–7.90 (m, 4 H); MS *m/z* M^+ 412 (100), M^+ + 1 (37), M^+ + 2 (16), 397 (14), 355 (17); HRMS *m/z* calcd for $C_{25}H_{36}O_3Si$ 412.2432, found 412.2410.

5-[(*tert*-Butyldimethylsilyl)oxy]-1,2,3,4,6,6a,12a,12b-octahydro-6-ethyl-9a-methyl-12*H*-benzo[*a*]xanthen-12-one (11j): yellow oil, 0.53 g (42%); ^1H NMR ($CDCl_3$) δ 0.16 (s, 3 H), 0.20 (s, 3 H), 0.92 (t, *J* = 1.2 Hz, 3 H), 0.95 (s, 9 H), 1.25 (s, 3 H), 1.50–2.35 (m, 10 H), 2.70–2.85 (m, 2 H), 4.10 (dd, *J* = 4.2 Hz, 1 H), 6.87–7.95 (m, 4 H); MS *m/z* M^+ 426 (100), M^+ + 1 (33), M^+

+ 2 (10), 411 (8.6), 369 (10); HRMS m/z calcd for $C_{28}H_{38}O_3Si$ 426.2588, found 426.2583.

4-[(*tert*-Butyldimethylsilyl)oxy]-2-(4-methyl-2-oxo-3-pentenyl)-2*H*-1-benzopyran (12): yellow oil, 0.56 g (85%); ^1H NMR ($CDCl_3$) δ 0.10 (s, 6 H), 0.88 (s, 9 H), 1.77 (d, J = 1.3 Hz, 3 H), 2.05 (d, J = 1.3 Hz, 3 H), 2.70 (dd, J = 14.7, 6.5 Hz, 1 H), 3.00 (dd, J = 14.7, 7.2 Hz, 1 H), 4.85 (d, J = 4.0 Hz, 1 H), 5.15-5.38 (m, 1 H), 5.94 (dd, J = 2.6, 1.3 Hz, 1 H), 6.50-7.30 (m, 4 H); HRMS m/z calcd for $C_{21}H_{30}O_3Si$ 358.1962, found 358.1942.

Protonolysis of 11c-cis and 11-trans. General Procedure. To a solution of 11c-cis (0.75 g, 1.84 mmol) in 3 mL of CH_2Cl_2 at room temperature was added a 10 mL of dilute HCl (10%). The mixture was stirred at room temperature for ca. 3 h, extracted with CH_2Cl_2, and washed sequentially with water. The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The crude solid was then recrystallized (CH_2Cl_2-hexane) to give 0.51 g (95%) of the corresponding ketone (13a-cis) as a colorless crystalline solid.

1,2,3,4,4a,9a-Hexahydro-1-phenyl-9*H*-xanthene-3,9-dione (13a-cis): colorless crystalline solid, 0.51 g (95%); mp 235-237 °C; ^1H NMR ($CDCl_3$) δ 2.65-3.00 (m, 4 H), 3.13 (dd, J = 10.3, 2.5 Hz, 1 H), 3.45-3.78 (m, 1 H), 4.95-5.08 (m, 1 H), 6.90-7.80 (m, 9 H); HRMS m/z calcd for $C_{19}H_{16}O_3$ 292.1089, found 292.1088. Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.90; H, 5.34.

1,2,3,4,4a,9a-Hexahydro-1-phenyl-9*H*-xanthene-3,9-dione (13b-trans): colorless crystalline solid, 0.25 g (82%); mp 182-184 °C; ^1H NMR ($CDCl_3$) δ 2.52-3.20 (m, 4 H), 3.26-3.65 (m, 2 H), 4.40-4.75 (m, 1 H), 6.90-7.80 (m, 9 H); HRMS m/z calcd for $C_{19}H_{16}O_3$ 292.1100, found 292.1102.

2-[[4-(*tert*-Butyldimethylsilyl)oxy]-2-methyl-(2*H*-1-benzopyran-2-yl)methyl]-4*H*-1-benzopyran-4-one (14). Treatment of 2d derived from 1d (0.21 g, 1.31 mmol) with 2,6-lutidine (0.15 mL, 1.31 mmol) in 4 mL of CH_2Cl_2 at room temperature gave 14 (0.26 g, 91%) as a colorless oil: IR (neat, cm^{-1}) 2900, 1640, 1600, 1570, 1380; ^1H NMR ($CDCl_3$) δ 0.15 (d, J = 1.0 Hz, 6 H), 0.98 (s, 9 H), 1.56 (s, 3 H), 2.95 (d, J = 1.5 Hz, 2 H), 4.83 (s, 1 H), 6.22 (s, 1 H), 6.75-7.11 (m, 7 H), 8.17 (dd, J = 6.4, 2.0 Hz, 1 H); MS m/z 434 (M^+); HRMS m/z calcd for $C_{28}H_{30}O_4Si$ 434.1912, found 434.1902.

Reaction of 2a,b with Isoprene (15a) and 2,3-Dimethylbutadiene (15b) (Table IV). General Procedure. To a solution of 2a derived from 1a (0.66 g, 4.52 mmol) in 10 mL of CH_2Cl_2 was added 2.26 mL (22.6 mmol) of isoprene at room temperature. After 5 h, the reaction mixture was poured into ice-cooled water (50 mL) and extracted with CH_2Cl_2 (30 mL × 3). The combined organic layers were dried ($MgSO_4$), concentrated, and purified with flash chromatography on silica gel (hexane-ethyl acetate = 5:1 as an eluent) to give 0.48 g (50%) of 16a as a yellow oil.

1,4,4a,9a-Tetrahydro-3-methyl-9*H*-xanthen-9-one (16a): yellow oil, 0.48 g (50%); ^1H NMR ($CDCl_3$) δ 1.67 (s, 3 H), 2.10-2.61 (m, 4 H), 2.73 (ddd, J = 8.4, 7.1, 2.7 Hz, 1 H), 4.76 (dt, J = 4.2, 2.7 Hz, 1 H), 5.49-5.58 (m, 1 H), 6.80-7.03 (m, 2 H), 7.42 (ddd, J = 8.5, 7.0, 1.9 Hz, 1 H), 7.84 (dd, J = 8.2, 1.9 Hz, 1 H); MS m/z M^+ 214 (85), M^+ + 1 (43), M^+ - 1 (68), 199 (100); HRMS m/z calcd for $C_{14}H_{14}O_2$ 214.0992, found 214.0981.

1,4,4a,9a-Tetrahydro-2,3-dimethyl-9*H*-xanthen-9-one (16b): yellow oil, 0.35 g (42%); ^1H NMR ($CDCl_3$) δ 1.76 (s, 6 H), 2.10-2.50 (m, 4 H), 2.81 (ddd, J = 9.4, 6.7, 2.8 Hz, 1 H), 4.76 (dt, J = 4.2, 2.8 Hz, 1 H), 6.80-7.03 (m, 2 H), 7.42 (ddd, J = 8.5, 7.0, 1.9 Hz, 1 H), 7.84 (dd, J = 8.5, 1.9 Hz, 1 H); MS m/z M^+ 228 (87.5), M^+ + 1 (44), M^+ - 1 (28), 213 (100), 195 (75); HRMS m/z calcd for $C_{15}H_{16}O_2$ 228.1148, found 228.1146. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 79.18; H, 7.30.

1,4,4a,9a-Tetrahydro-2,3,9a-trimethyl-9*H*-xanthen-9-one (16c): yellow oil, 0.18 g (25%); ^1H NMR ($CDCl_3$) δ 1.24 (s, 3 H), 1.67 (bs, 6 H), 2.34-2.61 (m, 4 H), 4.40 (t, J = 3.9 Hz, 1 H), 6.88-7.72 (m, 4 H); MS m/z M^+ 242 (77), M^+ + 1 (38), M^+ - 1 (11), 227 (50), 160 (100); HRMS m/z calcd for $C_{16}H_{18}O_2$ 242.1305, found 242.1300. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.41; H, 7.73.

Dehydrogenation of 16a: 3-Methylxanthone (17). To a solution of 16a (0.15 g, 0.70 mmol) in 4 mL of toluene was added p-toluenesulfonic acid (0.03 g) and DDQ (0.32 g, 1.40 mmol), and the mixture was heated at reflux with vigorous stirring for 3 h, cooled to room temperature, filtered, and concentrated. Purification by thin-layer chromatography using 20% ethyl acetate in hexane as eluent gave 0.11 g (75%) of 3-methylxanthone (17) as colorless solid: mp 94-95 °C (97 °C);[23] ^1H NMR ($CDCl_3$) δ 2.54 (s, 3 H), 7.23 (dd, J = 8.1, 1.5 Hz, 1 H), 7.30 (d, J = 1.5 Hz, 1 H), 7.37 (dt, J = 8.2, 1.7 Hz, 1 H), 7.48 (dd, J = 8.2, 1.7 Hz, 1 H), 7.72 (dt, J = 8.2, 1.7 Hz, 1 H), 8.23 (d, J = 8.1 Hz, 1 H), 8.34 (dd, J = 8.2, 1.7 Hz).

Acknowledgment. We are grateful to Dr. Hiroshi Hirota of the University of Tokyo for the measurement of high-resolution mass spectra. We thank Chisso Co., Ltd., for the gift of silyl chlorides, and the Grant-in-Aid for Scientific Research on Priority Areas, "Advanced Molecular Conversion (No. 63607522)" administered by the Ministry of Education, Science, and Culture of the Japanese Government.

Supplementary Material Available: ^1H NMR spectra for compounds 2a, 4a-c, 6a,c,d,f, 7a,b, 8a,b, 9a-c, 11a,b, 11c-cis, 11c-trans, 11d-h,j, 12, 13a,b, 14, and 16a-c; ^{13}C NMR spectra of compounds 11c-cis and 11c-trans (36 pages). Ordering information is given on any current masthead page.

(23) Goldberg, A. A.; Wragg, A. H. *J. Chem. Soc.* **1958**, 4227.

1,3-Elimination Reactions of (3,4-Epoxybutyl)stannanes. Approach to the Synthesis of Cycloeudesmol

Louis Plamondon[1] and James D. Wuest*

Département de Chimie, Université de Montréal, Montréal, Québec, H3C 3J7 Canada

Received March 28, 1990

The reactions that occur when stereochemically defined spirocyclic (3,4-epoxybutyl)stannanes are treated with $C_2H_5AlCl_2$ depend critically on the relative orientation of tin, oxygen, and the three connecting atoms of carbon. A W arrangement of these atoms tends to favor formation of cyclopropanes by a concerted 1,3-elimination with inversion at both carbon centers. If this orientation cannot be achieved, cleavage of the epoxide occurs to give an ionic intermediate that can undergo a subsequent 1,3-elimination or a 1,2-shift of hydride promoted by an antiperiplanar carbon-tin bond.

Loss of X^- from silane 1a or stannane 1b can trigger three characteristic reactions.[2-5] One is a 1,2-shift from the central carbon that leads to demetalation and formation of a derivative of propene (path a); another is a 1,3-

0022-3263/91/1956-2066$02.50/0