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Reactions of 4-Siloxy-1-benzopyrylium Salts with Allylsilane and Allylstannane Reagents

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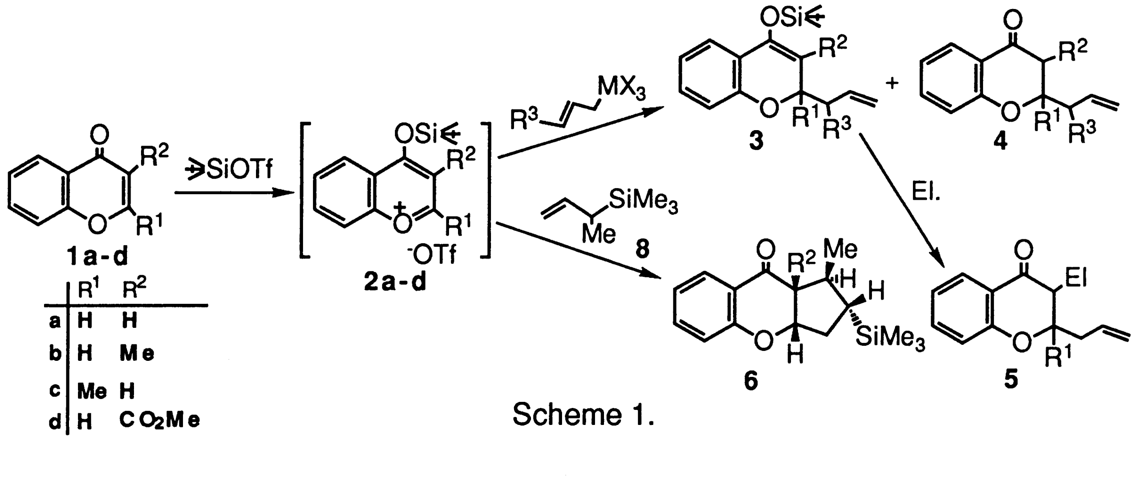
The reactions of allylstannanes with 4-siloxy-1-benzopyrylium salts gave the corresponding allylated derivatives more smoothly than allylsilanes. Similar reactions with 3-trimethylsilyl-1-butene afforded unexpected five-membered ring adducts in 87% and 37% yields, respectively.

Although 4*H*-1-benzopyran-4-one, chromone, derivatives **1** are a kind of α,β-unsaturated ketones, there are only a few synthetic methods for introduction of carbonucleophiles at C_2 position of the heterocycle, because there is an enol ether group within the heterocycle. Wallace et al. developed a convenient method for the above object by the aid of an electron-withdrawing group at C_3 position of pyrone ring.1) Recently we have demonstrated that silyl enol ethers reacted with siloxybenzopyrylium salts (**2a,b**) to give 2-substituted 4-siloxy-2*H*-1-benzopyran derivatives and [4+2] type cycloaddition products in high yield.2) We wish to report convenient allylation of chromones with allyl organometallic reagents and unexpected [3+2] type cyclization of **2a,b** with 3-trimethylsilyl-1-butene, which is effected by 1,2-silyl shift (Scheme 1).



	R¹	R²
a	H	H
b	H	Me
c	Me	H
d	H	CO₂Me

Scheme 1.

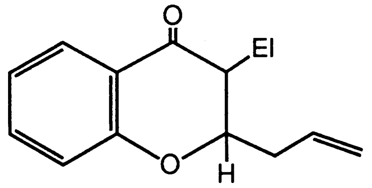
4-[(t-Butyldimethylsilyl)oxy]-1-benzopyrylium triflate (**2**) was prepared by heating an equimolar amount of the corresponding chromone and t-butyldimethylsilyl triflate (80 °C, ca. 1 h), the resulting **2** was dissolved in CH_2Cl_2 at room temperature for the following reactions.[2] Reaction of **2** with allyltrimethylsilane in the presence of 1 equiv. of 2,6-lutidine in CH_2Cl_2 solution afforded a mixture of 2-allyl-4-[(t-butyldimethylsilyl)oxy]-2*H*-1-benzopyran (**3a**) and 2-allyl-2,3-dihydro-4*H*-1-benzopyran-4-one (**4a**) in 22% and 12%, respectively.[3] In contrast to allyltrimethylsilane, reaction of **2a** with allyltributylstannane smoothly proceeded to give 2-allyl-4-siloxybenzopyran derivative **3a** in 85% yield (entry 1 vs. 4). These results are summarized in Table 1.

Table 1. Allylation of 4-Siloxy-1-benzopyrylium Salts **2a**-**d** with Allyl Organometallic Reagents

Entry	Compd.	R^1	R^2	R^3	MX_3	Product; Yield/%[a)] **3**	**4**
1	**2a**	H	H	H	$SiMe_3$	22(33)	12(18)
2	**2b**	H	Me	H	$SiMe_3$	0	43(64)
3	**2c**	Me	H	H	$SiMe_3$	0	0
4	**2a**	H	H	H	Sn*n*-Bu_3	85	0
5	**2b**	H	Me	H	Sn*n*-Bu_3	65	0
6	**2c**	Me	H	H	Sn*n*-Bu_3	15	0
7	**2a**	H	H	SPh	Sn*n*-Bu_3	62	0
8	**2b**	H	Me	SPh	Sn*n*-Bu_3	63	0
9	**2a**	H	H	H	$SnPh_3$	71	0
10	**2d**	H	CO_2Me	H	SiMe3	30	52
11	**2d**	H	CO_2Me	H	Sn*n*-Bu3	75	19

a) Isolated yields of products purified by preparative TLC. Spectral data were fully consistent with the assigned structures. The yields in parentheses are calculated based on the amount of the recovered starting material.

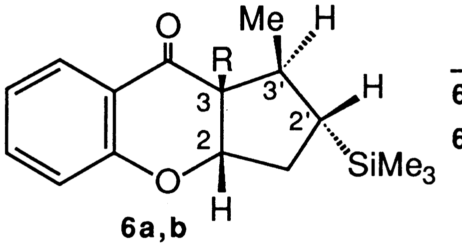
Allylation of **2a** with [3-(phenylthio)allyl]tributylstannane gave **3** under the equivalent conditions (entries 7, 8). Substitution at C_3 in chromone ring by a methoxycarbonyl group not only facilitated the formation of siloxypyrylium salt under milder conditions (70 °C, 30 min) but also activated the siloxypyrylium ions for the nucleophilic reaction (entries 10, 11). Bromination of **3a** with *N*-bromosuccinimide gave 2-allyl-3-bromo-2,3-dihydrobenzopyrone derivative **5a** in 37% yield.[3] Reaction of **3a** with 2,4-hexadienal ($ZnCl_2$ catalysis) afforded the siloxy aldol **5b** in 33% yield, where the silyl group was transferred to the resulting hydroxyl group.



5a,b

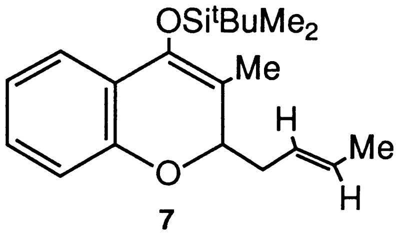
	El
5a	Br
5b	$CH_3(CH{=}CH)_2CH\,(OSi^tBuMe_2)$

On the other hand, treatment of **2a** with 3-trimethylsilyl-1-butene (**8**) provided the unexpected five-membered ring adduct **6a** in 87% yield.[3] In the reaction of **2b**, the corresponding cyclopentane annulation product **6b** (37% yield) was obtained along with allylated product as a minor product **7** (9% yield).[4] Stereochemistry of the cyclopentane annulation product **6a** was determined on the basis of the vicinal coupling constants. The small coupling constant of J_{H2H3} (J = 3.7 Hz) indicates that the relative stereochemistry of the two protons is equatorial-axial or cis geometry. The $H_{3'}$ hydrogen is trans to the H_3 as judged from the relatively large coupling constant ($J_{H3H3'}$= 10.8 Hz). Although the relative stereochemistry of silyl and methyl groups remains obscure from the vicinal coupling constant ($J_{H2'H3'}$ = 7.2 Hz), the trans geometry may be reasonable as described below.



6a,b

	R
6a	H
6b	Me



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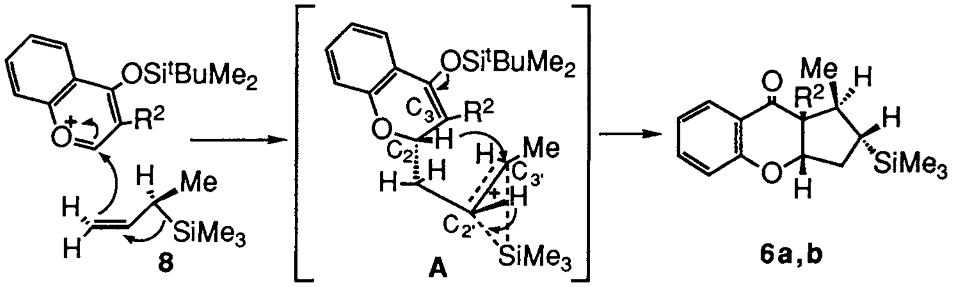
The mechanism for this cycloaddition is outlined in Scheme 2. The allyl reagent **8** attacks the siloxypyrylium salts **2a,b** at 2-position giving the intermediate carbocation **A** which is stabilized by the trimethylsilyl and the methyl groups. Attack by the emerging silyl enolate at $C_{3'}$ forms the five-membered ring compounds **6a,b**. Generally, electrophiles attack allylic silanes at γ position and from anti direction to the silyl group.[5] Since there is undoubtedly interaction of the emerging cation with the silicon in the transition state, the stereochemistry of the bridged intermediate **A** should be trans geometry due to stereoelectronic effect and allylic 1,3-strain.[6] The stereochemistry of ring junction (cis relationship) is also consistent with that expected from this consideration.

Usually, the carbocations such as **A** is desilylated by the chloride ion generated in situ to produce olefins. In the reaction of **2a**, the favored pathway was cyclization. The competition between cyclization and desilylation in the case of **2b** would be due to the steric hindrance between the two methyl groups at the step of cyclization. This type of cyclization has been observed in reaction of allylstannanes with α,β-unsaturated acyliron complexes.[7]



Scheme 2.

References

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3) Spectral data: **3a** : colorless oil ; ^{1}H NMR (CDCl$_3$) δ 0.06 (s, 3H), 0.10 (s, 3H), 0.99 (s, 9H), 2.35-2.65 (m, 2H), 4.79 (d, J = 3.5 Hz, 1H), 4.92 (dd, J = 6.2, 3.5 Hz, 1H), 5.00-5.30 (m, 2H), 5.61-6.00 (m, 1H), 6.60-6.90 (m, 2H), 7.10 (dt, J = 7.5, 1.8 Hz, 1H), 7.32 (dd, J = 7.5, 1.8 Hz, 1H). Mass ; m/z 302 (M^+), 259 (base peak). **4a** : colorless oil ; ^{1}H NMR (CDCl$_3$) δ 2.48-2.95 (m, 4H), 4.55-5.60 (m, 1H), 5.08-5.55 (m, 2H), 5.88 (ddt, J = 17.7, 9.6, 6.8 Hz, 1H), 6.80-7.02 (m, 2H), 7.42 (ddd, J = 8.5, 7.0, 1.9 Hz, 1H), 7.84 (dd, J = 8.2, 1.9 Hz, 1H). Mass ; m/z 188 (M^+), 147 (base peak). **5a** : yellow oil ; ^{1}H NMR (CDCl$_3$) δ 2.40-3.00 (m, 2H), 4.21 (ddd,J = 7.5, 6.6, 1.8 Hz, 1H), 4.40 (d, J = 1.8 Hz, 1H), 5.05-5.40 (m, 2H), 5.90 (dddd, J = 17.4, 7.9, 7.9, 5.9 Hz, 1H), 6.83-7.02 (m, 2H), 7.42 (ddd, J = 8.5, 7.0, 1.9 Hz, 1H), 7.84 (dd, J = 8.2, 1.9 Hz, 1H). Mass ; m/z 266 (M^+), 227. **6a** : colorless oil ; ^{1}H NMR (CDCl$_3$) δ 0.03 (s, 9H), 0.85 (d, J = 7.2 Hz, 3H), 1,27 (ddd, J = 12.9, 7.2, 7.2 Hz, 1H), 1.67 (ddd, J = 12.9, 12.9, 3.7 Hz, 1H), 2.33 (dd, J = 12.9, 7.2 Hz, 1H), 2.54 (ddq, J = 10.8, 7.2, 7.2 Hz, 1H), 2.77 (dd, J = 10.8, 3.7 Hz, 1H), 4.93 (dd, J = 3.7, 3.7 Hz, 1H), 6.80-7.02 (m, 2H), 7.42 (ddd, J = 8.5, 7.0, 1.9 Hz, 1H), 7.84 (dd, J = 8.3, 1.9 Hz, 1H). Mass ; m/z 274 (M^+), 259. Anal. Calcd for $C_{16}H_{22}O_2Si$ C, 70.03; H, 8.08. Found C, 69.99; H, 8.32.

4) **7**: Only one isomer was isolated. The 2-butenyl group at C_2 is trans ($J_{H2'H3'}$ = 15.0 Hz).

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