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The Formation of Oxygen-Containing Heterocycles via Intramolecular Cyclizations of Halo-substituted Acylsilanes and Unsaturated Acylsilanes

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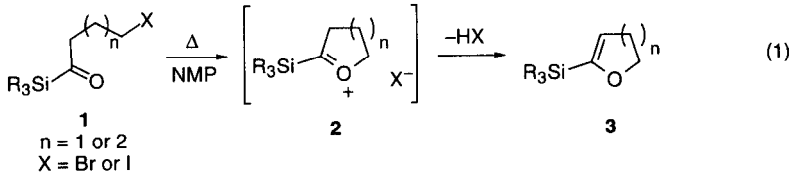
Abstract: Halo-substituted acylsilanes undergo cyclizations easily when heated in a polar solvent such as NMP to afford 2-silyldihydrofurans and 2-silyldihydropyrans. Unsaturated acylsilanes undergo cyclizations through reactions with iodine, phenylselenenyl bromide, or chloride. Further reactions of the cyclized products with pyridinium perbromide, phenylselenenyl bromide, or chloride give highly functionalized dihydrofurans and dihydropyrans.

Keywords: Cyclization; Furans; Pyrans; Silicon and compounds.

Acylsilanes exhibit interesting physical and chemical properties,[1] sparking continued interest in the synthesis and synthetic application of this class of compounds. Synthetically there are two highly distinct features of acylsilanes. The first one is the high electrophilic nature of the carbonyl carbon of acylsilanes, in which the large silyl group is often used as a handle for stereoselective transformations.[1,2] The second one is the existence of several rearrangement possibilities, either directly by photolysis or heating,[1,3] or through nucleophilic attacks.[1,4] Recently, acylsilanes have been found to be excellent radical acceptors.[5]



1 (n = 1 or 2, X = Br or I) **2** **3** (1)

Several years ago we reported the ionic cyclization of halogen substituted acylsilanes give dihydrofurans or dihydropyrans.[6,7] As shown in eq 1, this process presumably involves a nucleophilic attack of the carbonyl oxygen at the halogen substituted carbon.[8] In contrast, aldehydes and ketones do not undergo this similar type of reaction easily, and basic conditions are often used.[9] This difference may be attributed to the higher basicity

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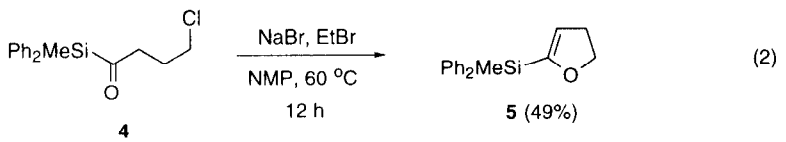
of the carbonyl oxygen in acylsilanes.[10] Recently, Molander and Siedem reported the cyclization of acylsilane aldehydes generates furans.[11] The cyclizations of bisacylsilanes under acidic conditions were studied by Saleur, Bouillon, and Portella.[12] Herein we wish to report the full account of our study on the ionic cyclizations of acylsilanes to produce oxygen-containing heterocycles.

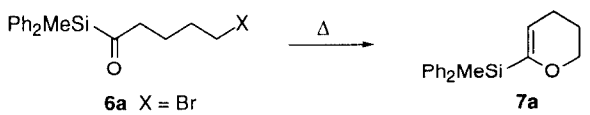
RESULTS AND DISCUSSION

For the purpose of the study of radical cyclizations of acylsilanes,[5] we needed to prepare a bromide from γ-chloroacylsilane **4** (eq 2) via the method developed by Lukevics and coworkers.[13] Surprisingly, heating chloride **4**[5a] with sodium bromide in *N*-methylpyrrolidone (NMP) at 60 °C (12 h) in the presence of excess ethyl bromide afforded dihydrofuran **5** in 49% yield. We found that this type of cyclization is quite general for the bromine substituted acylsilanes. As shown in Table 1 (entry 1), heating bromoacylsilane **6a**[5a] in NMP at 100 °C for 13 h gives dihydropyran **7a** in 91% yield. In contrast, bromide **6a** is stable in refluxing THF or benzene overnight (entries 7, 8). Therefore, the use of a polar solvent such as NMP is crucial for the success of the cyclization. The cyclization reaction can also be carried out in DMF (entry 3). Although the reaction proceeds in acetonitrile (entry 5), the rate is too slow to be useful. Because the cyclization reaction also produces one equivalent of hydrogen bromide, we can use one equivalent of triethylamine as an acid sponge (entries 2, 4, 6). It is noteworthy that 2-silyldihydropyran is quite stable in the presence of hydrogen bromide as in the case of entry 1 (Table 1).



4 **5** (49%) (2)

Table 1. The effect of solvent and triethylamine on the cyclization of bromoacylsilane **6a**.



6a X = Br **7a**

entry	solvent	Et_3N (equiv)	temp (°C)	time (h)	yield (%)
1	NMP	0	100	13	91
2	NMP	1	100	6	79
3	DMF	0	100	9	79
4	DMF	1	100	5	75
5	CH_3CN	0	81	23	42[a]
6	CH_3CN	1	81	48	55[b]
7	THF	0	65	7	–[c]
8	Benzene	0	80	8	–[c]

[a]Recovered 10% bromide **6a**. [b]Recovered 13% bromide **6a**. [c]No reaction.

Table 2. The effect of different halides on the efficiency of the haloacylsilane cyclization.

entry	substrate	solvent	KI (equiv)	temp (°C)	time (h)	yield of **7a** (%)
1	**6b** X = Cl	DMF	0	100	72	39
2	**6b**	DMF	catalytic	100	48	53
3	**6b**	NMP	1	100	48	97
4	**6b**	NMP	2	100	16	94
5	**6c** X = I	benzene	0	80	16	22[a]

[a]Recovered 53% of **6c**.

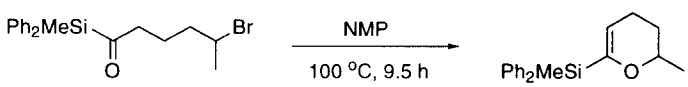
In contrast to the cyclization of bromoacylsilane **6a**, chloroacylsilane **6b** (Table 2, entry 1) is less reactive. However, in the presence of potassium iodide (entries 2–4, Table 2), the cyclization of **6b** can eventually be accomplished in a reasonably short time with high yield. In fact, iodoacylsilane **6c** (entry 5, Table 2) undergoes cyclization even in refluxing benzene albeit in low efficiency.

To prepare dihydrofuran **5** from chloroacylsilane **4**, we treated **4** with one equivalent of potassium iodide in NMP at 100 °C for 12 h (entry 1, Table 3). Surprisingly, we did not obtain any dihydrofuran **5** (cf. entry 3, Table 2). With a lower temperature (66 °C) and longer time (entry 2), we were able to isolate dihydrofuran **5** in 72% yield. This indicates that the five-membered ring product may be sensitive to the reaction condition at high temperature, and that lower temperature and shorter reaction time are preferred. Therefore, with the addition of more potassium iodide (3 equiv) the reaction was completed in 8 h at 70 °C with excellent yield (entry 3).

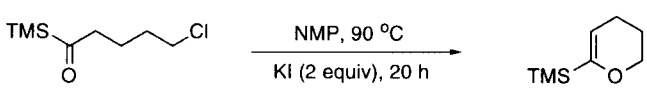
Table 3. Formation of dihydrofuran **5** from the cyclization of chloroacylsilane **4**.

entry	solvent	KI (equiv)	temp (°C)	time (h)	yield of **5** (%)
1	NMP	1	100	12	0
2	NMP	1	66	30	72
3	NMP	3	70	8	94

This type of cyclization reaction is not limited to primary halides. As shown in eq 3, the secondary bromide **8**[5a] cyclized in NMP at 100 °C for 9.5 h resulted in an 83% yield of dihydropyran **9**. The silyl group of the acylsilane can be changed to a presumably labile trimethylsilyl group in chloroacylsilane **10** (eq 4). The cyclization of **10** proceeded in NMP at 90 °C (20 h) in the presence of two equivalents of potassium iodide to produce a 71% yield of dihydropyran **7b**.[14]

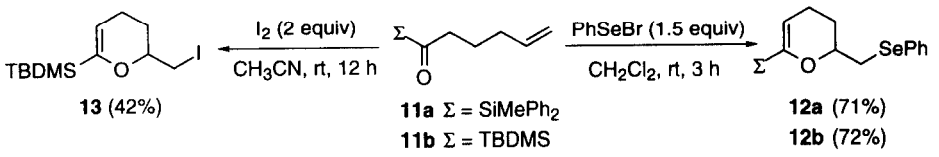


8 **9** (83%) (3)



10 **7b** (71%) (4)

Scheme 1

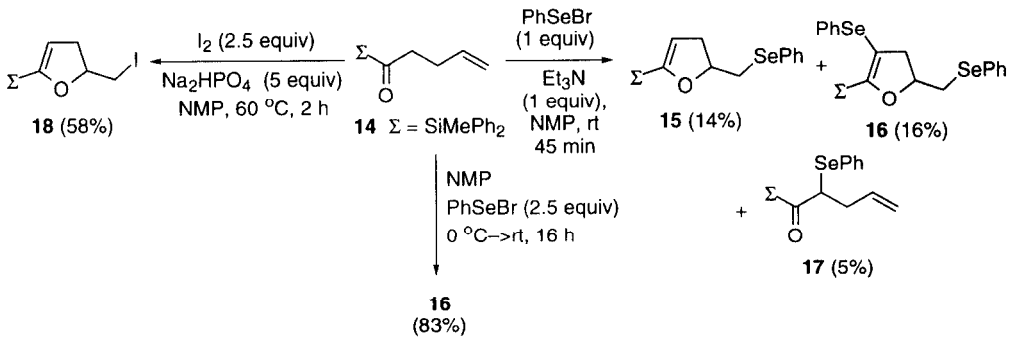


13 (42%) **11a** Σ = $SiMePh_2$ **12a** (71%)
11b Σ = TBDMS **12b** (72%)

Olefin initiated cyclization is a common strategy used to prepare oxygen-containing heterocycles.[15] The carbonyl functional groups that participate in these type of reactions include amides, carboxylic acids, and esters. Due to the unusual nucleophilic nature of the carbonyl oxygen of acylsilanes, we also studied the olefin initiated cyclization of unsaturated acylsilanes. The unsaturated acylsilanes can be prepared using the 1,3-dithiane strategy developed by Brook and Corey.[16,17] Indeed, acylsilanes **11a**[17] and **11b** (Scheme 1) reacted with phenylselenenyl bromide (1.5 equiv) in dichloromethane at room temperature (3 h) to afford selenides **12a** (71%) and **12b** (72%), respectively. Furthermore, treatment of unsaturated acylsilane **11b** with iodine (2 equiv) in acetonitrile at room temperature for 12 h generated cyclized iodide **13** in 42% yield.

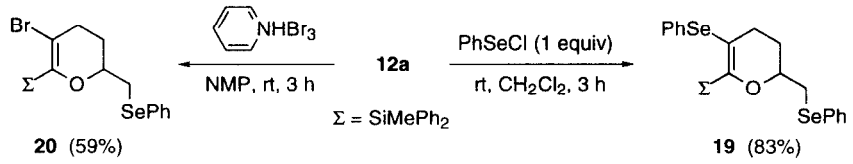
In contrast, the reaction of homologous acylsilane **14** (Scheme 2) with 1.1 equivalent of phenylselenenyl bromide in dichloromethane (rt, 3 h) did not produce any cyclized product . When the polar solvent NMP was used (Scheme 2), acylsilane **14** reacted with one equivalent of phenylselenenyl bromide in the presence of triethylamine (1 equiv) at room temperature (45 min) to give a mixture of monoselenide **15** (14%), bis-selenide **16** (16%), and acylsilane **17** (5%). Treatment of monoselenide **15** with another equivalent of phenylselenenyl bromide led to the formation of bis-selenide **16**.[18] In principle, bis-selenide **16** may also be originated from further cyclization of acylsilane **17**. Therefore, we reacted acylsilane **14** with 2.5 equivalent of phenylselenenyl bromide in NMP at 0 °C, warmed it up to room temperature (16 h), and obtained 83% yield of bis-selenide **16**. We found that under various conditions it is very difficult to obtain the monoselenide without the formation of the bis-selenide. Iodide **18** can also be prepared (58%) by reacting acylsilane **14** with excess iodine (2.5 equiv) in NMP at 60 °C (2 h). Sodium hydrogen phosphate (5 equiv) was used to remove hydrogen iodide. In the iodination reaction, we did not have the problem of over-iodination. In comparison, dihydropyran **12a** (Scheme 3) was treated with phenylselenenyl chloride (1 equiv) in dichloromethane to give bis-selenide **19** in

Scheme 2



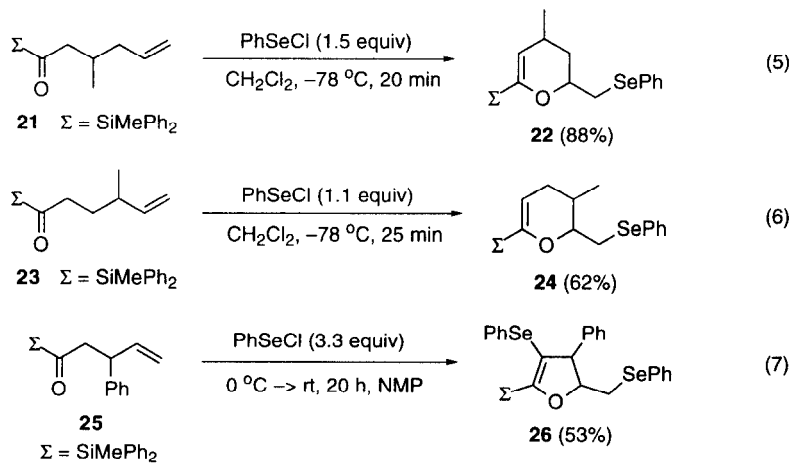
18 (58%) **14** Σ = $SiMePh_2$ **15** (14%) **16** (16%)
17 (5%)
16 (83%)

Scheme 3



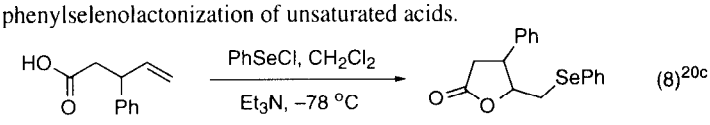
83% yield. Bromination is also possible, and the reaction of dihydropyran **12a** with pyridinium perbromide in NMP produced a 59% yield of vinyl bromide **20**.[19]

In general, the formation of the dihydropyran from the unsaturated acylsilane is easier than dihydrofuran. This difference is probably due to the higher strain endured in the 5-membered ring formation. The formation of dihydrofuran is best performed in polar solvents such as NMP. However, for phenyl-selenenylation, it is difficult for the five-membered ring system to stop at the monoselenenylation. This also reflects the slower rate of dihydrofuran formation, and other side reactions become competitive. The six-membered ring system can be performed in a less polar solvent, namely dichloromethane, and the mono-selenenylation can be accomplished. In the case of acylsilane **14**, 6-*endo-trig* cyclizations are not observed. This indicates the kinetic nature of the cyclizations. The regioselectivity is also in accordance to the general trend observed in olefine initiated cyclizations.[15,20]



To examine the degree of diastereoselectivity of substituted olefinic acylsilane cyclizations, we studied the cyclizations of acylsilanes **21**, **23**, and **25**[21] (eq 5–7). Both **21** (eq 5) and **23** (eq 6) reacted with phenylselenyl chloride (1.1 equiv) in dichloromethane at –78 °C and formed dihydropyran selenides **22** (88%) and **24** (62%) as 1:1 and 2.2:1 diastereomeric mixtures, respectively. When the cyclization of acylsilane **21** was performed at room temperature, the isomeric ratio of dihydropyran **22** did not change. The cyclization of acylsilane **25**, carried out in NMP with 3.3 equivalents of phenylselenyl chloride (eq 7), gave dihydrofuran **26** in 53% yield as a 2:1 mixture of *cis/trans* isomers. We did not determine which isomer is the major one. Comparing with the

phenylselenolactonization, 3-phenyl-4-pentenoic acid (**27**) was reported to give *cis*- and *trans*-lactone **28** (eq 8) in a ratio of 1:2.7, respectively.[20c] Similarly, the analogous 6-membered ring lactone formation also showed low diastereoselectivity.[22,23] The unsaturated acylsilane cyclizations do not provide better stereocontrol than the corresponding phenylselenolactonization of unsaturated acids.



27 54% **28** (8)[20c]

In summary, bromo-substituted acylsilanes easily undergo cyclizations when heat in a polar solvent such as NMP to afford 2-silyldihydrofurans and 2-silyldihydropyrans. The cyclizations of chloroacylsilanes are slower; however, the efficiency of the cyclizations can be enhanced by the addition of potassium iodide. Unsaturated acylsilanes undergo cyclizations in the presence of iodine, phenylselenenyl bromide, or chloride. When there is a substituent at the β- or γ-position, the cyclizations of unsaturated acylsilanes give very little diastereoselectivity. Further reactions of the cyclized products with pyridinium perbromide, phenylselenenyl bromide, or chloride are possible. Through this method, highly functionalized dihydrofurans and dihydropyrans can be prepared.

EXPERIMENTAL SECTION

^{1}H NMR spectra were recorded at 200 or 300 MHz; ^{13}C NMR spectra were recorded at 50 or 75 MHz. Tetramethysilane (δ = 0 ppm) or $CHCl_3$ (δ = 7.24 ppm) were used as internal standards and $CDCl_3$ was used as the solvent. Benzene and THF were distilled from sodium benzophenone ketyl under N_2. Dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), and acetonitrile were dried over calcium hydride. Acetone was distilled over sodium carbonate. All reactions were performed under a blanket of N_2 or Ar.

5-Chloro-1-(methyldiphenylsilyl)pentan-1-one (6b). To a solution of 340 mg of 2-methyldiphenylsilyl-1,3-dithiane[5a] (1.1 mmol) in 1.0 mL of THF cooled in an ice-water bath was added dropwise over 6 min 1.0 mL of a 1.49 M solution of *n*-butyllithium in hexane (1.5 mmol). After stirring for another 30 min at 0 °C, the resulting solution was cooled in a dry ice-acetonitrile bath followed by the addition of 0.16 mL (1.6 mmol) of 1-bromo-3-chloropropane in one portion. The resulting mixture was stirred at the same temperature for 1 h and then partitioned between 30 mL of ether and 20 mL of water. The organic layer was washed with 20 mL of brine, dried ($MgSO_4$) and concentrated *in vacuo*. The residual oil was dissolved in 7 mL of wet THF (15%) followed by the addition of 350 mg (1.6 mmol) of red mercuric oxide, 210 mg of Celite, and 0.20 mL (1.6 mmol) of borontrifluoride etherate. The resulting mixture was stirred at room temperature for 2 h, diluted with ether (50 mL) and filtered. The filtrate was washed with brine (10 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The residual oil was chromatographed over silica gel (eluted with hexane/ethyl acetate = 98/2) to give 252 mg (77%) of **6b** as a pale yellow oil: IR (neat) 1640 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.75 (s, 3 H, $SiCH_3$), 1.55–1.75 (m, 4 H), 2.68 (br t, *J* = 7 Hz, 2 H, $COCH_2$), 3.40 (br t, *J* = 7 Hz, 2 H, $ClCH_2$), 7.25–7.50 (m, 6 H), 7.50–7.68 (m, 4 H); ^{13}C NMR (50 MHz) δ −5.5, 19.4, 31.8, 44.5, 48.4, 128.1, 130.1, 132.5, 134.9, 243.6; mass spectrum, *m/z* (relative intensity) 315 (M^+−1, 3), 225 (25), 197 (100), 181 (15), 105 (20), 85 (30). Anal. Calcd for $C_{18}H_{21}ClOSi$: C, 68.22; H, 6.68. Found: C, 68.50; H, 5.93.

5-Iodo-1-(methyldiphenylsilyl)pentan-1-one (6c). A solution of 90.0 mg (0.28 mmol) of **6b** and 60 mg (0.40 mmol) of sodium iodide in 2 mL of acetone was stirred under argon at 60 °C for 2 h. The resulting mixture was diluted with ether and filtered. The filtrate was concentrated in vacuo to give 101 mg (89%) of crude **6c** as a yellow oil. This material will decompose through silica gel column chromatography and was used directly for the cyclization. IR (neat) 1640 cm^{-1}; ^1H NMR (200 MHz) δ 0.75 (s, 3 H, $SiCH_3$), 1.50–1.75 (m, 4 H), 2.66 (t, J = 7 Hz, 2 H, $COCH_2$), 3.04 (t, J = 7 Hz, 2 H, ICH_2), 7.30–7.50 (m, 6 H), 7.50–7.63 (m, 4 H); ^{13}C NMR (50 MHz) δ −5.4, 6.2, 23.0, 32.8, 48.1, 128.2, 130.1, 132.4, 134.9, 243.6.

5-Chloro-1-(trimethylsilyl)pentan-1-one (10). According to the procedure for the preparation of **6b**, we prepared **10** (84%) as a pale yellow oil: IR (neat) 1639 cm^{-1}; ^1H NMR (200 MHz) δ 0.20 (s, 9 H, CH_3), 1.55-1.85 (m, 4 H), 2.64 (t, J = 7 Hz, 2 H, $COCH_2$), 3.52 (t, J = 6 Hz, 2 H, $ClCH_2$); ^{13}C NMR (50 MHz) δ −3.4, 19.2, 31.9, 44.5, 47.1, 247.2; mass spectrum, *m/z* (relative intensity) 193 (M^+, 10), 119 (5), 93 (20), 73 (100), 55 (30); HRMS calcd for $C_8H_{18}{}^{35}ClOSi$ *m/z* 193.0815, found 193.0771.

General procedure for the cyclizations of haloacylsilanes. The haloacylsilane (1 mmol) was dissolved in 10 mL of dried NMP and heated with the reagents at the temperature and time indicated in Tables 1–3 and eq 3, 4. The resulting solution was partitioned between 50 mL of ether and 50 mL of water. The ether layer was washed with brine (20 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The residue was chromatographed over silica gel column chromatography (eluted with suitable ethyl acetate/hexane pair) to give the desired product.

5-Methyldiphenylsilyl-2,3-dihydrofuran (5). IR (neat) 1590 cm^{-1}; ^1H NMR (200 MHz) δ 0.69 (s, 3 H, $SiCH_3$), 2.63 (td, J = 10, 2 Hz, 2 H, allyl), 4.36 (t, J = 10 Hz, 2 H, OCH_2), 5.30 (t, J = 2 Hz, 1 H, =CH), 7.25–7.50 (m, 6 H), 7.50–7.70 (m, 4 H); ^{13}C NMR (50 MHz) δ −4.6, 30.7, 70.8, 115.4, 127.8, 129.6, 134.4, 134.9, 159.0. Anal. Calcd for $C_{17}H_{18}OSi$: C, 76.64; H, 6.81. Found: C, 76.92; H, 6.89.

6-Methyldiphenylsilyl-3,4-dihydro-2*H*-pyran (7a). IR (neat) 1611 cm^{-1}; ^1H NMR (200 MHz) δ 0.62 (s, 3 H, $SiCH_3$), 1.87 (quintet, J =5 Hz, 2 H), 2.03 (q, J =5 Hz, 2 H, allyl), 3.95 (t, J =5 Hz, 2 H, OCH), 5.05 (t, J =5 Hz, 1 H, =CH), 7.20–7.40 (m, 6 H), 7.50–7.65 (m, 4 H); ^{13}C NMR (50 MHz) δ −4.9, 20.9, 22.6, 65.7, 114.9, 127.7, 129.3, 135.0, 135.3, 157.0; mass spectrum, *m/z* (relative intensity) 280 (M^+, 30), 197 (100), 180 (25), 137 (40), 105 (50), 53 (40); HRMS calcd for $C_{18}H_{20}OSi$ *m/z* 280.1284, found 280.1283.

2-Methyl-6-methyldiphenylsilyl-3,4-dihydro-2*H*-pyran (9). IR (neat) 1611 cm^{-1}; ^1H NMR (200 MHz) δ 0.62 (s, 3 H, $SiMe_3$), 1.26 (d, J = 7 Hz, 3 H, O-C-CH_3), 1.50–1.69 (m, 2 H), 1.75–2.16 (m, 2 H), 3.85–4.01 (m, 1 H, OCH), 5.02 (t, J = 4 Hz, 1 H, =CH), 7.28–7.50 (m, 6 H), 7.50–7.69 (m, 4 H); ^{13}C NMR (50 MHz) δ −4.9, 21.1, 29.3, 29.7, 71.0, 114.1, 127.6, 129.2, 134.0, 135.1, 135.7, 156.6; mass spectrum, *m/z* (relative intensity) 294 (M^+, 100), 279 (6), 251 (18), 237 (9), 215 (8), 197 (98), 156 (38), 137 (75); HRMS calcd for $C_{19}H_{22}OSi$ *m/z* 294.1441, found 294.1435.

General procedure for the preparation of unsaturated acylsilanes. To a solution of the 2-silyl-1,3-dithiane (3.0 mmol) in 3.0 mL of THF cooled in an ice-water bath was added dropwise over 5 min 2.4 mL of a 1.50 M solution of *n*-butyllithium in hexane (3.6 mmol). After stirring for another 30 min at 0 °C, the unsaturated bromide (3.6 mmol) was added dropwise over 5 min. The resulting mixture was stirred at the same temperature for 1 h and then partitioned between 50 mL of ether and 20 mL of water. The organic layer was washed with 20 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was mixed with 800 mg of Celite, and 500 mg of sodium bicarbonate in 7 mL of acetonitrile/water (3/1 by volume) and cooled in an dry ice-carbon tetrachloride bath. A solution of ceric ammonium nitrate (12 mmol) in 12 mL of acetonitrile/water (3/1 by volume) was added over 3 min to the above mentioned mixture. The resulting mixture was stirred at the same temperature for another 3 min, diluted with 20 mL of ether, and filtered. The filtrate was washed with 10 mL of water, 10 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was chromatographed over silica gel column chromatography (eluted with suitable ethyl acetate/hexane pair) to give the unsaturated acylsilane.

1-*t*-Butyldimethylsilyl-5-hexen-1-one (11b). According to the general procedure, the reaction of 2-*t*-butyldimethylsilyl-1,3-dithiane with 5-bromopentene gave 64% of **11b** as a pale yellow oil: IR (neat) 1637 cm^{-1}; ^1H NMR (300 MHz) δ 0.13 (s, 6 H, $SiCH_3$), 0.89 (s, 9 H, *t*-butyl), 1.57 (quintet, *J* = 7 Hz, 2 H, CO-C-CH_2), 1.97 (quartet, *J* = 7 Hz, 2 H, allyl), 2.56 (t, *J* = 7 Hz, 2 H, $COCH_2$), 4.88–5.00 (m, 2 H, $=CH_2$), 5.71 (ddt, *J* =17, 10, 7 Hz, 2 H, CH=); ^{13}C NMR (75 MHz) δ –7.0, 16.4, 20.9, 26.4, 33.1, 49.3, 115.0, 138.2, 246.5; mass spectrum, *m/z* (relative intensity) 211 (M^+–1, 5), 159 (24), 147 (19), 115 (50), 91 (20), 75 (59), 73 (100), 69 (8); HRMS calcd for $C_{12}H_{23}OSi$ (M^+–1) *m/z* 211.1513, found 211.1494.

1-Methyldiphenylsilyl-4-penten-1-one (14). According to the general procedure, the reaction of 2-methyldiphenylsilyl-1,3-dithiane[5a] with 4-bromobutene gave 57% of **14** as a pale yellow oil: IR (neat) 1637 cm^{-1}; ^1H NMR (300 MHz) δ 0.77 (s, 3 H, $SiCH_3$), 2.23 (q, *J* = 7 Hz, 2 H, allyl), 2.77 (t, *J* = 7 Hz, 2 H, $COCH_2$), 4.86–4.98 (m, 2 H, $=CH_2$), 5.72 (ddt, *J* =17, 10, 7 Hz, 1 H, CH=), 7.36–7.45 (m, 6 H), 7.56–7.63 (m, 4 H); ^{13}C NMR (50 MHz) δ –5.4, 26.1, 48.7, 114.9, 128.2, 130.1, 132.5, 134.9, 137.3, 243.3; mass spectrum, *m/z* (relative intensity) 279 (M^+–1, 2), 265 (2), 251 (5), 238 (6), 225 (30), 197 (100), 142 (7), 137 (27); HRMS calcd for $C_{18}H_{20}OSi$ *m/z* 280.1284, found 280.1273.

3-Methyl-1-methyldiphenylsilyl-5-hexen-1-one (21). According to the general procedure, the reaction of 2-methyldiphenylsilyl-1,3-dithiane[5a] with 5-bromo-4-methylpentene[24] gave 51% of **21** as a pale yellow oil: IR (neat) 1639 cm^{-1}; ^1H NMR (300 MHz) δ 0.72 (s, 3 H, $SiCH_3$), 0.76 (d, *J* = 7 Hz, 3 H, CH_3), 1.70–1.95 (m, 2 H, allyl), 2.10 (octet, *J* = 7 Hz, 1 H, CHMe), 2.44 (dd, *J* = 17, 7 Hz, 1 H, $COCH_2$), 2.65 (dd, *J* = 17, 7 Hz, 1 H, $COCH_2$), 4.84–4.95 (m, 2 H, $=CH_2$), 5.58 (ddt, *J* =17, 10, 7 Hz, 1 H, CH=), 7.24–7.47 (m, 6 H), 7.47–7.65 (m, 4 H); ^{13}C NMR (75 MHz) δ –5.3, 19.8, 27.3, 41.1, 56.2, 116.2, 128.2, 130.1, 132.8, 135.0, 136.7, 244.7; mass spectrum, *m/z* (relative intensity) 308 (M^+, 1), 197 (100), 137 (32); HRMS calcd for $C_{20}H_{24}OSi$ *m/z* 308.1596, found 308.1586.

4-Methyl-1-methyldiphenylsilyl-5-hexen-1-one (23). According to the general procedure, the reaction of 2-methyldiphenylsilyl-1,3-dithiane[5a] with 5-bromo-3-methylpentene[25] gave 48% of **23** as a pale yellow oil:

IR (neat) 1620 cm^{-1}; ^1H NMR (300 MHz) δ 0.73 (s, 3 H, $SiCH_3$), 0.88 (d, J = 7 Hz, 3 H, CH_3), 1.32–1.60 (m, 2 H), 1.97 (septet, J = 7.5 Hz, 1 H, allyl), 2.62 (t, J = 7.5 Hz, 2 H, $COCH_2$), 4.72–4.88 (m, 2 H, $=CH_2$), 5.49 (dt, J =15, 7.5 Hz, 1 H, CH=), 7.30–7.45 (m, 6 H), 7.51–7.59 (m, 4 H); ^{13}C NMR (50 MHz) δ −5.3, 20.2, 28.5, 37.4, 47.4, 113.2, 127.5, 128.0, 128.2, 130.0, 132.9, 135.0, 143.8, 244.4; mass spectrum, *m/z* (relative intensity) 308 (M^+, 9), 293 (20), 266 (18), 231 (19), 197 (100), 170 (19), 137 (28); HRMS calcd for $C_{20}H_{24}OSi$ *m/z* 308.1596, found 308.1604.

6-Methyldiphenylsilyl-2-phenylselenenylmethyl-3,4-dihydro-2*H*-pyran (12a). A solution of 70 mg (0.24 mmol) of **11a** and 83 mg (0.36 mmol) of phenylselenenyl bromide in 1.5 mL of dichloromethane was stirred at room temperature for 3 h and then partitioned between 20 mL of ether and 20 mL of water. The organic layer was washed with 10 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residual oil was chromatographed over silica gel (eluted with dichloromethane/hexane = 15/85) to give 76 mg (71%) of **12a** as a pale yellow liquid: IR (neat) 1610 cm^{-1}; ^1H NMR (300 MHz) δ 0.61 (s, 3 H, $SiCH_3$), 1.62–1.83 (m, 1 H), 1.91–2.18 (m, 3 H), 3.02 (dd, J = 12.4, 6.6 Hz, 1 H, SeCH), 3.17 (dd, J = 12.4, 6.2 Hz, 1 H, SeCH), 3.93–4.05 (m, 1 H, OCH), 5.03 (br s, 1 H, =CH), 7.12–7.24 (m, 3 H), 7.30–7.42 (m, 6 H), 7.42–7.48 (m, 2 H), 7.56–7.60 (m, 4 H); ^{13}C NMR (75 MHz) δ −4.9, 20.8, 27.0, 32.4, 74.2, 114.5, 126.6, 127.7, 130.0, 132.3, 135.1, 156.6; mass spectrum, *m/z* (relative intensity) 250 (M^+, 29), 293 (47), 197 (100), 137 (28); HRMS calcd for $C_{25}H_{26}OSeSi$ *m/z* 450.0928, found 450.0920.

6-*t*-Butyldimethylsilyl-2-phenylselenenylmethyl-3,4-dihydro-2*H*-pyran (12b). According to the procedure for the preparation of **12a**, the reaction of 119 mg (0.56 mmol) of **11b** and 198 mg (0.84 mmol) phenylselenenyl bromide gave 149 mg (72%) of **12b** as a pale yellow oil: IR (neat) 1612 cm^{-1}; ^1H NMR (200 MHz) δ 0.02 (s, 6 H, $SiCH_3$), 0.90 (s, 9 H, *t*-Bu), 1.55–1.75 (m, 1 H), 1.85–2.15 (m, 3 H), 2.99 (dd, J = 12, 6 Hz, 1 H, SeCH), 3.17 (dd, J = 12, 6 Hz, 1 H, SeCH), 3.83-3.95 (m, 1 H, OCH), 4.94 (br t, J = 4 Hz, 1 H, =CH), 7.15–7.28 (m, 3 H), 7.45–7.52 (m, 1 H), 7.55–7.65 (m, 1 H); ^{13}C NMR (50 MHz) δ −7.0, 16.5, 20.7, 26.7, 27.3, 32.7, 73.7, 111.4, 126.6, 127.7, 129.0, 129.2, 131.4, 132.1, 158.5; mass spectrum, *m/z* (relative intensity) 368 (M^+, 18), 311 (100), 234 (15), 215 (93), 195 (6), 157 (30), 115 (13), 73 (97), 59 (23); HRMS calcd for $C_{18}H_{28}OSeSi$ *m/z* 368.1074, found 368.1069.

6-*t*-Butyldimethylsilyl-2-iodomethyl-3,4-dihydro-2*H*-pyran (13). To a solution of 106 mg (0.50 mmol) of **11b** in 2.5 mL of acetonitrile at room temperature was added over 5 min a solution of 254 mg (1.0 mmol) of iodine in 2 mL of acetonitrile. The resulting solution was stirred for another 12 h and partitioned between 10 mL of ether and 10 mL of water. The ether layer was washed with 10 mL of sat. sodium thiosulfate aqueous solution, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was chromatographed over silica gel (eluted with ethyl acetate/hexane = 2/98) to give 66 mg (42%) of **13** as a pale yellow oil: IR (neat) 1615 cm^{-1}; ^1H NMR (200 MHz) δ 0.25 (s, 6 H, $SiCH_3$), 0.90 (s, 9 H, *t*-Bu), 1.56–1.73 (m, 1 H), 1.85–2.15 (m, 3 H), 3.23 (d, J = 6 Hz, 2 H, ICH), 3.66-3.77 (m, 1 H, OCH), 4.90–4.98 (m, 1 H, =CH); ^{13}C NMR (50 MHz) δ −7.0, 9.1, 16.5, 20.3, 26.8, 27.3, 73.4, 111.2, 158.4; mass spectrum, *m/z* (relative intensity) 338 (M^+, 11), 281 (76), 211 (8), 185 (100), 153 (28), 79 (13), 75 (90), 59 (21), 43 (17); HRMS calcd for $C_{12}H_{24}IOSi$ (M^++1) *m/z* 339.0643, found 339.0683.

5-Methyldiphenylsilyl-4-phenylselenenyl-2-phenylselenenylmethyl-2,3-dihydrofuran (16). To a solution of 200 mg (0.71 mmol) of **14** in 3 mL of NMP cooled in an ice-water bath was added 419 mg (1.80 mmol) of phenylselenenyl bromide in one portion. The resulting solution was stirred at room temperature for 16 h and partitioned between 25 mL of ether and 25 mL of water. The ether layer was washed with 10 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was chromatographed over silica gel (eluted with ethyl acetate/hexane = 4/96) to give 348 mg (83%) of **16** as a yellow oil: IR (neat) 1573 cm^{-1}; ^1H NMR (300 MHz) δ 0.83 (s, 3 H, $SiCH_3$), 2.62 (dd, J = 15.8, 7.0 Hz, 1 H, allyl), 2.94 (dd, J = 15.8, 10.1 Hz, 1 H, allyl), 3.03 (d, J = 12.3 Hz, 1 H, SeCH), 3.22 (dd, J = 12.3, 5.0 Hz, 1 H, SeCH), 4.75–4.87 (m, 1 H, OCH), 7.10–7.27 (m, 8 H), 7.28–7.58 (m, 8 H), 7.57–7.63 (m, 4 H); ^{13}C NMR (50 MHz) δ −3.0, 33.0, 42.7, 81.5, 114.0, 126.4, 127.1, 127.8, 129.0, 129.6, 130.7, 133.0, 134.7, 135.1; mass spectrum, *m/z* (relative intensity) 591 (M^+−1, 12), 590 (12), 197 (100); HRMS calcd for $C_{30}H_{28}OSe_2Si$ *m/z* 592.0240, found 592.0220.

2-Iodomethyl-5-methyldiphenylsilyl-2,3-dihydrofuran (18). A mixture of 50 mg (0.18 mmol) of **14**, 115 mg (0.45 mmol) of iodine, and 130 mg (0.92 mmol) of sodium hydrogen phosphate in 1.5 mL of NMP was heated at 60 °C for 2 h. The resulting mixture was partitioned between 25 mL of ether and 25 mL of sat. sodium thiosulfate aqueous solution. The ether layer was dried ($MgSO_4$), and concentrated *in vacuo*. The residue was chromatographed over silica gel (eluted with dichloromethane/hexane = 1/4) to give 42 mg (58%) of **18** as a yellow oil: IR (neat) 1594 cm^{-1}; ^1H NMR (200 MHz) δ 0.69 (s, 3 H, $SiCH_3$), 2.48 (ddd, J = 16.0, 6.5, 2.5 Hz, 1 H, allyl), 2.83 (ddd, J = 16.0, 10.0, 2.2 Hz, 1 H, allyl), 3.23 (dd, J = 10.0, 8.0 Hz, 1 H, ICH), 3.33 (dd, J = 10.0, 4.0 Hz, 1 H, ICH), 4.65–4.82 (m, 1 H, OCH), 5.20 (br s, 1 H, =CH), 7.32–7.46 (m, 6 H), 7.55–7.66 (m, 4 H); ^{13}C NMR (75 MHz) δ −4.7, 10.4, 36.9, 81.3, 114.1, 127.9, 129.7, 134.5, 134.9, 158.5; mass spectrum, *m/z* (relative intensity) 406 (M^+, 50), 279 (30), 197 (100); HRMS calcd for $C_{18}H_{19}IOSi$ *m/z* 406.0250, found 406.0248.

6-Methyldiphenylsilyl-5-phenylselenenyl-2-phenylselenenylmethyl-3,4-dihydro-2*H*-pyran (19). A solution of 83 mg (0.18 mmol) of **12a** and 36 mg (0.19 mmol) of phenylselenenyl chloride in 1.0 mL of dichloromethane was stirred at room temperature for 3 h and then partitioned between 20 mL of ether and 20 mL of water. The organic layer was washed with 10 mL of brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residual oil was chromatographed over silica gel (eluted with dichloromethane/hexane = 15/85) to give 91 mg (83%) of **19** as a yellow liquid: IR (neat) 1572 cm^{-1}; ^1H NMR (200 MHz) δ 0.77 (s, 3 H, $SiCH_3$), 1.70–1.92 (m, 1 H), 2.00–2.50 (m, 3 H), 2.99 (dd, J = 12.4, 6.6 Hz, 1 H, SeCH), 3.17 (dd, J = 12.4, 6.4 Hz, 1 H, SeCH), 3.98–4.14 (m, 1 H, OCH), 7.00–7.18 (m, 5 H), 7.18–7.42 (m, 9 H), 7.42–7.56 (m, 2 H), 7.56–7.75 (m, 4 H); ^{13}C NMR (50 MHz) δ −1.7, 28.6, 29.1, 32.1, 74.1, 115.1, 126.0, 126.9, 127.5, 128.7, 129.0, 130.2, 130.4, 132.6, 135.1, 136.1; mass spectrum, *m/z* (relative intensity) 606 (M^+, 64), 604 (57), 602 (31), 197 (100); HRMS calcd for $C_{31}H_{31}OSeSi$ *m/z* 606.0396, found 606.0392.

5-Bromo-6-methyldiphenylsilyl-2-phenylselenenylmethyl-3,4-dihydro-2*H*-pyran (20). According to the procedure for the preparation of **19**, the reaction of 55 mg (0.12 mmol) of **12a** and 40 mg (0.12 mmol) of pyridinium perbromide in 1 mL of NMP gave 38 mg (59%) of **20** as an unstable yellow oil: ^1H NMR (200 MHz) δ 0.78 (s, 3 H, $SiCH_3$), 1.70–2.06 (m, 1 H), 2.06–2.16 (m, 1 H), 2.30–2.65 (m, 2 H), 2.92 (dd, J =

12.5, 6.6 Hz, 1 H, SeCH), 3.07 (dd, J = 12.5, 6.4 Hz, 1 H, SeCH), 3.83–4.00 (m, 1 H, OCH), 7.10–7.23 (m, 3 H), 7.23–7.50 (m, 8 H), 7.50–7.65 (m, 4 H); ^{13}C NMR (50 MHz) δ −2.3, 28.8, 31.7, 32.1, 74.0, 113.2, 127.0, 127.6, 129.1, 129.3, 132.5, 135.2, 153.1. This bromide is unstable, and we were not able to obtain satisfactory analysis.

4-Methyl-6-methyldiphenylsilyl-2-phenylselenenylmethyl-3,4-dihydro-2*H*-pyran (22). According to the procedure for the preparation of **12a**, the reaction of 27 mg (0.088 mmol) of **21** and 23 mg (0.097 mmol) of phenylselenenyl bromide in 0.5 mL of dichloromethane at −78 °C for 20 min gave 35 mg (88%) of **22** as a yellow oil. This material is a 1:1 mixture of two diastereomers: IR (neat) 1613 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.61 (s, 3 H, $SiCH_3$), 0.90–1.00 (two overlapped d, J = 6.9 Hz, at 0.95 and 0.97, 3 H, CH_3), 1.33 (q, J = 11.5 Hz, 1 H of isomer A), 1.63 (br d, J = 12 Hz, 1 H of isomer B), 1.80–1.95 (m, 1 H of isomer B), 2.07 (br dd, J = 11.5, 6.3 Hz, 1 H of isomer A), 2.10–2.29 (m, 1 H of isomer B), 2.30–2.47 (m, 1 H of isomer A), 2.95–3.55 (m, 1 H, SeCH), 3.10–3.22 (m, 1 H, SeCH), 3.92–4.08 (m, 1 H, OCH), 4.88 (br s, 1 H, =CH of isomer A), 5.02 (br s, 1 H of isomer B), 7.10–7.21 (m, 3 H), 7.24–7.48 (m, 8 H), 7.53–7.65 (m, 4 H). Anal. Calcd for $C_{26}H_{28}OSeSi$: C, 67.37; H, 6.09. Found: C, 67.02; H, 6.02.

3-Methyl-6-methyldiphenylsilyl-2-phenylselenenylmethyl-3,4-dihydro-2*H*-pyran (24). According to the procedure for the preparation of **12a**, the reaction of 30 mg (0.097 mmol) of **23** and 21 mg (0.10 mmol) of phenylselenenyl chloride in 1.0 mL of dichloromethane at −78 °C for 20 min gave 28 mg (62%) of **24** as a yellow oil. This material is a 2.2:1 mixture of two diastereomers: IR (neat) 1610 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.63 (s, 3 H, $SiMe_3$), 0.92 (d, J = 6.5 Hz, 2.2 H, CH_3 of the minor isomer), 0.96 (d, J = 6.5 Hz, 0.8 H, CH_3 of the major isomer), 1.65–1.78 (m, 1 H), 1.95–2.18 (m, 1.7 H), 2.25–2.36 (m, 0.3 H), 2.90 (dd, J = 12.3, 5.7 Hz, 0.3 H, SeCH of the minor isomer), 3.10–3.26 (m, 1.7 H), 3.76 (q, J = 7.1 Hz, 0.7 H, OCH of the major isomer), 4.00–4.08 (m, 0.3 H, OCH of minor isomer), 4.98 (br s, 0.3 H, =CH of the minor isomer), 5.03 (br s, 0.7 H, =CH of the major isomer), 7.12–7.25 (m, 3 H), 7.25–7.42 (m, 6 H), 7.42–7.52 (m, 2 H), 7.56–7.68 (m, 4 H); mass spectrum, m/z (relative intensity) 464 (M^+, 53), 387 (21), 307 (52), 197 (100), 137 (20), 83 (76); HRMS calcd for $C_{21}H_{26}O_2Si$ m/z 464.1074, found 464.1076.

5-Methyldiphenylsilyl-3-phenyl-4-phenylselenenyl-2-phenylselenenylmethyl-2,3-dihydrofuran (26). According to the procedure for the preparation of **16**, the reaction of 200 mg (0.562 mmol) of **25**[19] and 360 mg (1.88 mmol) of phenylselenenyl chloride in 2.0 mL of NMP and stirred at room temperature for 20 h to give 197 mg (53%) of **26** as a yellow oil. This material is a 2:1 mixture of two diastereomers: IR (neat) 1572 cm^{-1}; ^{1}H NMR (300 MHz) major isomer: δ 1.03 (s, 3 H, $SiCH_3$), 3.20 (dd, J = 12.3, 7.7 Hz, 1 H, SeCH), 3.37 (dd, J = 12.3, 5.0 Hz, 1 H, SeCH), 3.96 (d, J = 4.9 Hz, 1 H, PhCH), 4.80–4.90 (m, 1 H, OCH), 7.12–7.45 (m, 13 H), 7.45–7.60 (m, 8 H), 7.74–7.90 (m, 4 H); characteristic signals for the minor isomer: δ 1.05 (s, 3 H, $SiCH_3$), 2.79 (dd, J = 12.6, 7.8 Hz, 1 H, SeCH), 3.11 (dd, J = 12.6, 7.5 Hz, SeCH), 4.10 (d, J = 7.5 Hz, 1 H, PhCH), 5.02 (q, J = 7.5 Hz, 1 H, OCH); mass spectrum, m/z (relative intensity) 669 (M^+, 26), 354 (34), 197 (100), 157 (25); HRMS calcd for $C_{36}H_{32}OSe_2Si$ m/z 668.0633, found 668.0593.

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