Swern Oxidation of Alkenyl-Substituted 2-(*tert*-Butyldimethylsiloxy)-1-(hydroxymethyl)cyclopropanes: A Novel and Flexibel Route to Functionalized 2,5-Dihydrooxepines

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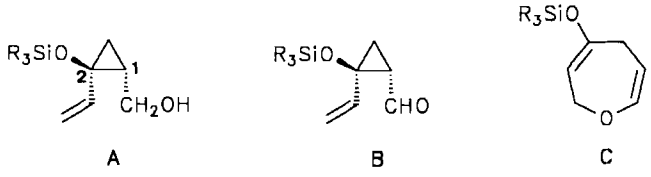
Swern oxidation of 2-alkenyl-substituted 2-siloxy-1-(hydroxymethyl)cyclopropanes **7** and **11**–**16** provided 2,5-dihydrooxepines **8** and **17**–**21**, respectively. The corresponding cyclopropanecarboxaldehydes are highly plausible intermediates in this transformation, which give the seven-membered heterocycles by a concerted [3,3]-sigmatropic rearrangement. Some of the 2,5-dihydrooxepines easily undergo ring contraction to 2-vinyl-2,3-dihydrofurans. Direct formation of these furan derivatives was observed when (hydroxymethyl)-cyclopropanes **25**–**28** were oxidized. In these cases a stepwise rearrangement of the 2-siloxycyclopropanecarboxaldehydes involving 1,3-zwitterions as intermediates is proposed. Our results are compared with the few literature examples and reveal interesting substituent effects. Thus, the donor-acceptor substitution shifts the equilibrium between the 2-vinylcyclopropanecarboxaldehydes and the 2,5-dihydrooxepines to the side of the seven-membered heterocycles. Further mechanistic details are discussed.

In the preceding publication we described the diastereoselective preparation of alkenyl-substituted 2-(*tert*-butyldimethylsiloxy)-1-(hydroxymethyl)cyclopropanes **A** which are easily and flexibly available from the corresponding methylcyclopropane-carboxylates[2]. Compounds **A** were synthesized with the aim to convert them into cyclopropanecarboxaldehydes **B** which should be interesting intermediates for a number of useful transformations, e.g. Wittig reactions for the generation of divinylcyclopropane derivatives[3]. However, in orientating experiments we realized that aldehydes **B** cannot be isolated – instead, 2,5-dihydrooxepines **C** were obtained. This ring system is of high interest and a matter of numerous current synthetic efforts[4] due to its occurrence in a variety of natural products including polycyclic marine toxins[5] such as ciguatoxin[6] or brevetoxin B[7] as the most spectacular examples. Therefore, we undertook a more systematic study to reveal scope and limitations of the sequence **A** → **B** → **C** and mechanistic details of the process **B** → **C**[8].



Results

In order to prove the applicability of possible oxidation methods[9] we started with the more easily accessible (hydroxymethyl)cyclopropanes **1** and **4**. As expected, compound **1** was smoothly transformed into aldehyde **2** under standard conditions of the Swern oxidation[10]. However, although formed in almost quantitative yield, **2** could not be purified since distillation caused rearrangement to 2,3-dihydrofuran derivative **3**. Similarly, Swern oxidation of alcohol **4** provided a mixture of cyclopropanecarboxaldehyde **5** and 2,3-dihydrofuran derivative **6** (ratio 9:1) which could be completely converted into **6** by heating to 40°C for 2 h. These experiments demonstrated that the Swern method for oxidations is mild enough to generate cyclopropanecarboxaldehyde, but they also indicate that the products are rather sensitive and prone to rearrangement. Similar isomerizations of cyclopropanecarboxaldehydes had earlier been observed by Wenkert et al.[11].

Applicaton of these oxidation conditions to the most simple 2-alkenyl-substituted 2-(*tert*-butyldimethylsiloxy)-1-(hydroxymethyl)cyclopropane **7** provided neither the expected aldehyde nor the corresponding 2,3-dihydrofuran derivative but the isomeric 2,5-dihydrooxepine **8** in quantitative yield. Although the crude product was rather pure according to NMR spectroscopy, purification of this sensitive compound – and that of the other oxepine derivatives described in this report – turned out to be cumbersome, and large amounts of the material were always lost[12]. An attempt to remove impurities by brief extraction with 2 N HCl led to isomerization to 2,3-dihydrooxepine **9**, and chromatography on basic alumina surprisingly afforded the ring-contracted 2,3-dihydro-2-vinylfuran **10**. Finally, it was

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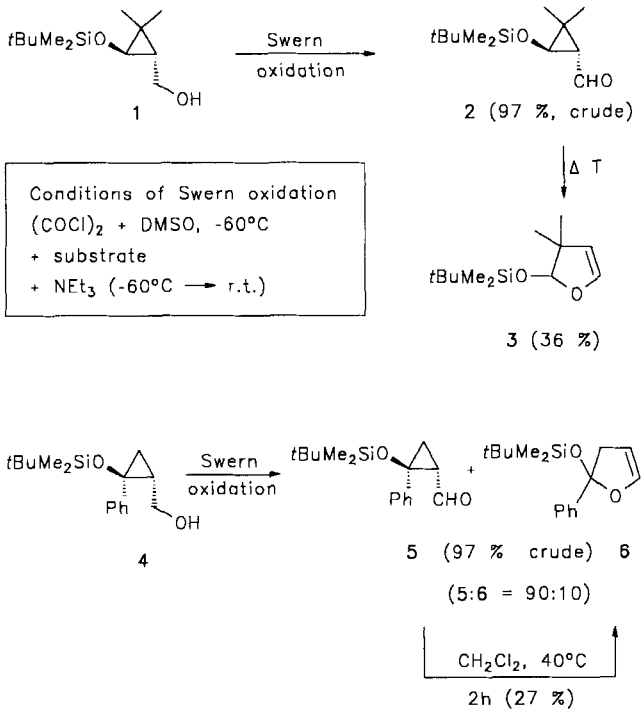
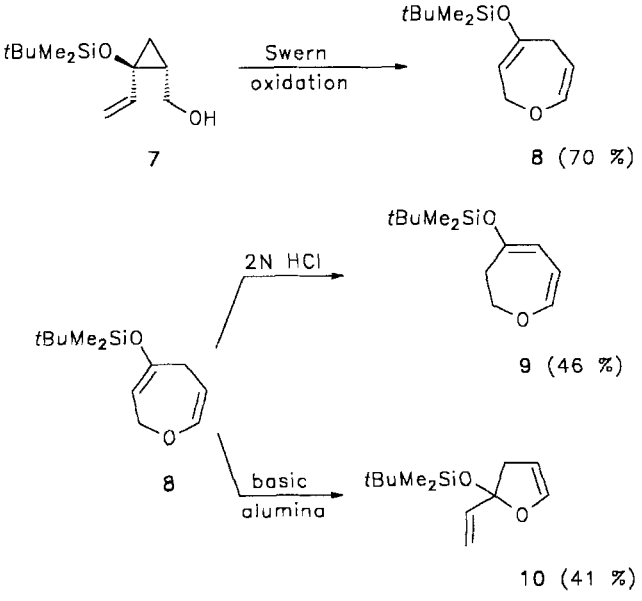
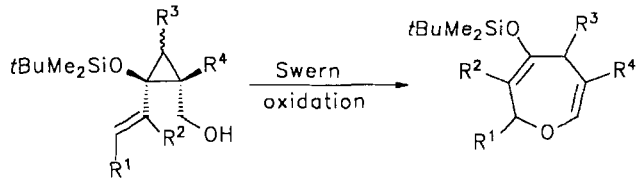


found that precipitation of polar impurities by brief treatment of the crude product with pentane and fast distillation gave 2,5-dihydrooxepines with reasonable purity in most cases.



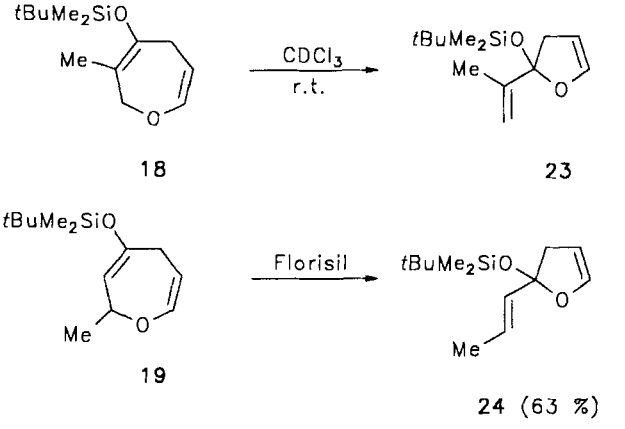
The Swern oxidations performed with (hydroxymethyl)-cyclopropanes **11**–**16** furnished the 2,5-dihydrooxepines **17**–**22** in moderate to good yields, thus demonstrating that a fairly general entry to these heterocycles has been found. Compound **19** was only characterized as crude product due to its particular sensitivity to rearrangement to 2,3-dihydrofuran derivative **24**. It was also observed that 2,5-dihydrooxepine **18** during storage in $CDCl_3$ very easily isomerized to 2,3-dihydrofuran **23**.

The formation of 2,5-dihydrooxepines is unambiguously proved by inspection of ^1H- and ^{13}C-NMR data. Thus, for compound **8** the endocyclic enol ether unit is shown by proton signals at $\delta = 4.25$ (6-H) and 6.18 (7-H) and the silyl enol ether moiety causes a signal at $\delta = 5.09$ (3-H). The corresponding carbon atoms of these alkene units are represented by signals at $\delta = 98.1$ (C-6), 146.8 (C-7), 101.9 (C-3), and 160.7 (C-4). On the other hand, 2-alkenyl-2,3-dihydrofurans show the typical signals for an unconjugated alkenyl group and the endocyclic enol ether.



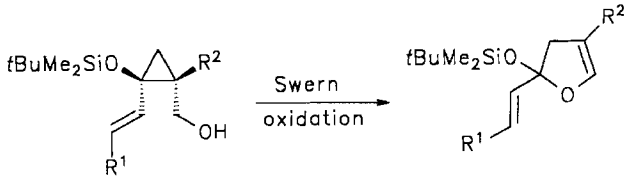
	R^1	R^2	R^3	R^4		Yield
11	H	H	Me	H	17	79 %
12	H	Me	H	H	18	63 %
13	Me	H	H	H	19	87 % [a]
14	H	H	H	Me	20	49 %
15	H	H	H	Allyl	21	70 %
16	H	Me	H	Me	22	44 %

[a] Crude product, showed partial isomerization to 24 during workup.



Our experiments show that isopropenyl- and propenyl-substituted cyclopropanes such as **12**, **13**, and **16** still give the expected 2,5-dihydrooxepines although these seem to be more sensitive with respect to ring contraction. On the other hand, the styryl-substituted compounds **25**–**27** and the methoxyvinyl-substituted cyclopropane **28** were converted into 2,3-dihydrofuran derivatives **29**–**32** exclusively when exposed to the Swern oxidation. Compound **32** was very sensitive and decomposed during purification. If the oxidation of (hydroxymethyl)cyclopropane **25** was followed

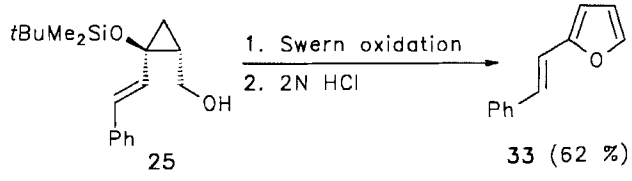
by treatment with acid, 1-furyl-2-phenylethene (**33**) was isolated in moderate yield – apparently formed by elimination from **29**.



25 - 28 29 - 32

	R^1	R^2		Yield
25	Ph	H	29	70 %
26	Ph	Me	30	68 %
27	p-$CF_3C_6H_4$	H	31	61 %
28	MeO	H	32	93 % [a]

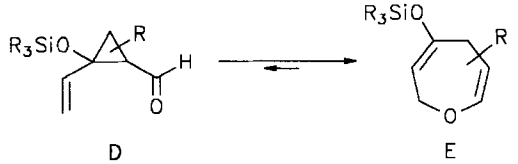
[a] Crude product, showed complete decomposition during chromatographical workup.



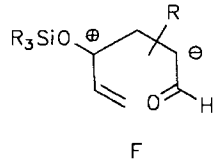
25 33 (62 %)

Discussion

As shown by the isolation of aldehydes **2** and **5**, Swern oxidation of all (hydroxymethyl)cyclopropanes investigated must have provided the corresponding cyclopropanecarboxaldehydes as primary products. For 2-alkenyl-substituted derivatives **D** – as generated from **7** and **11**–**16** – a fast concerted Cope-type [3,3]-sigmatropic reaction, which may also be classified as retro Claisen rearrangement, can be assumed for the formation of 2,5-dihydrooxepines **E**. This process is allowed as concerted reaction[13] due to the *cis* location of the aldehyde and alkenyl groups, and thus a rearrangement at room temperature or even below is possible. A stepwise mechanism involving a reasonable stabilized 1,3-zwitterion **F** has also to be considered, but seems less likely; formation of this intermediate generally requires higher activation as indicated by the rearrangement of aldehyde **5** to dihydrofuran **6** (see discussion below).



D E

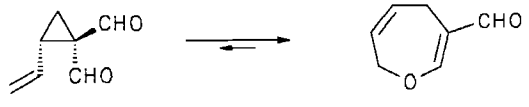


F

A few related[14] examples for the rearrangement of vinylcyclopropanecarboxaldehydes to 2,5-dihydrooxepines are reported in the literature, but, surprisingly, in most cases the equilibria of these reversible reactions are on the cyclopropane side despite the ring strain. Thus, the unsubstituted parent compound shows a distribution of 95:5 in favour of vinylcyclopropanecarboxaldehyde[14] at room temperature. That substituents can strongly influence the equilibrium was demonstrated by Brook et al. with a chlorinated derivative[14]. In our examples we never found spectroscopic evidence for the participation of vinylcyclopropanecarboxaldehydes **D**. We assume that the thermodynamic preference for the 2,5-dihydrooxepines **E** is caused by the donor-acceptor situation in the cyclopropane, which should weaken the central C–C bond[15] and therefore destabilize **D**. On the other hand, the enol ether resonance in **E** stabilizes the ring-enlarged compound.

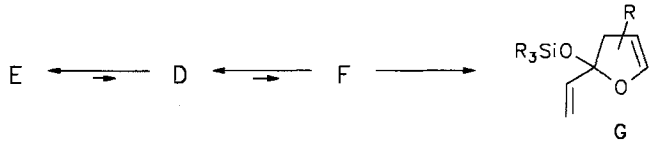
Complementary to these substituent effects are those found by Boeckman et al.[16] who very recently published that vinylcyclopropanecarboxaldehydes such as **34** bearing additional acceptor groups also furnish 2,5-dihydrooxepines, e.g. **35**. In these examples the equilibria are driven to the large ring systems by the stability of the donor-acceptor alkene moiety.

2-Phenyl-2-vinylcyclopropanecarboxaldehyde[1] apparently is at borderline, since its rearrangement to the corresponding 4-phenyl-2,5-dihydrooxepine is rather slow and not quantitative. After distillation (60°C) a 28:72 mixture of aldehyde and oxepine derivative was obtained[1]. Thus, a phenyl group is not sufficient to drive the equilibrium completely to the side of the seven-membered heterocycle.



34 35

Rearrangements of cyclopropanecarboxaldehydes **2** and **5** probably involve 1,3-zwitterions similar to **F** as intermediate[17] since the concerted pathway as suprafacial [1,3]-sigmatropic process is forbidden[18]. Formation of 2-alkenyl-2,3-dihydrofurans **10** and **23** from their isomeric 2,5-dihydrooxepines **8** and **18**, respectively, is most plausibly interpreted by equilibria of the oxepine derivatives **E** with the corresponding cyclopropanecarboxaldehydes **D** (as discussed above) followed by a stepwise rearrangement via 1,3-zwitterions **F** to the thermodynamically more stable furan derivatives **G**. Interestingly, this process is catalyzed (in a somewhat unpredictable fashion) by base (Al_2O_3) or acid (unpurified $CDCl_3$), observations for which precedence in related reactions could be found in the literature[18].

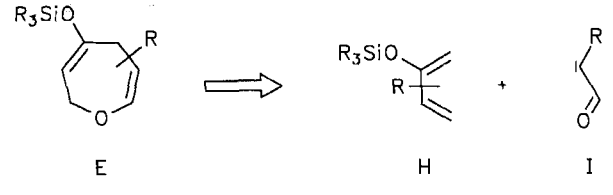


G

Styryl-substituted and 2-methoxyalkenylcyclopropanecarboxaldehydes as generated by oxidation of **25**–**28** "directly" afforded 2,3-dihydrofurans **29**–**32** without indication of 2,5-dihydrooxepine formation. These 2,3-dihydrofuran derivatives are apparently formed very rapidly according to pathway **D** → **F** → **G**, and it is questionable whether oxepines **E** are involved in these reactions. Their formation should be kinetically disfavoured by steric repulsion due to the terminal substituent at the alkenyl unit, and, in addition, by thermodynamic reasons because of resonance loss between the double bond and the aryl (or methoxy) group. On the other hand, these substituents stabilize the positive charge in 1,3-zwitterion **F**, and therefore in these examples the stepwise [1,3]-rearrangement may actually override the concerted [3,3]-process due to more favourable kinetics and thermodynamics.

In summary, the stability of isomers seems to increase in the order 2-vinylcyclopropanecarboxaldehyde **D** ≪ 2,5-dihydrooxepine **E** < 2-vinyl-2,3-dihydrofuran **G**, and the seven-membered heterocycles are only formed because they are kinetically favoured. In this context it is also interesting to note that methyl 2-vinyl-2-siloxycyclopropanecarboxylates are thermally stable up to at least 150°C[2,20] whereas the corresponding aldehydes described here rearrange at room temperature or even below.

2,5-Dihydrooxepines **E** have formally been constructed by a [4 + 3] cycloaddition of siloxy dienes **H** and formyl carbens **I**. This overall transformation could be put into practice by the sequence [2 + 1] cycloaddition, conversion ester → aldehyde, and [3,3]-sigmatropic rearrangement. Although our study reveals some limitations with respect to the substitution patterns achievable, this route to 2,5-dihydrooxepines may be of synthetic interest since the functionalities in this heterocycle allow several transformations. Orientating experiments exploring these possibilities will be reported in due course[21].



E H I

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Experimental

For general remarks see ref.[22]. – NMR: in $CDCl_3$ at 300 MHz (^1H) and 75.5 MHz (^{13}C). – $(COCl)_2$ was commercially available (Merck) and was used as obtained. DMSO was dried with molecular sieves and NEt_3 was distilled from CaH_2.

General Procedure: The oxidation of (hydroxymethyl)cyclopropanes was performed according to the original procedure described by Swern[10]. Dry DMSO (2.2 mmol/mmol cyclopropane) was added to a cooled (−60°C) solution of $(COCl)_2$ (1.1 eq.) in dry CH_2Cl_2 (2.5 ml/mmol cyclopropane), and the mixture was stirred for 5 min. During 5 min, a solution of the (hydroxymethyl)cyclopropane in CH_2Cl_2 was added dropwise, and the mixture was stirred for further 15 min. After addition of 5 eq. of NEt_3 the mixture was stirred for 15 min, before the cooling bath was removed and the mixture was stirred for 3 h. After addition of water (5 ml/mmol cyclopropane) the layers were separated, and the organic phase was washed with water for several times. The combined organic layers were dried ($MgSO_4$), and the solvent was removed in vacuo. The crude product was dissolved in pentane and the solution refluxed for 30 min. The pentane layer was separated, and pentane was then evaporated in vacuo. The remaining residue was purified by kugelrohr distillation.

Oxidation of 2-(tert-Butyldimethylsiloxy)-1-(hydroxymethyl)-3,3-dimethyl-cyclopropane (**1**): 1.15 g (5.00 mmol) of **1**, dissolved in 5 ml of CH_2Cl_2, was allowed to react at −60°C with a mixture of 0.720 g (5.67 mmol) of $(COCl)_2$, dissolved in 12.5 ml of CH_2Cl_2, and 0.860 g (11.0 mmol) of DMSO as described in the general procedure, and 2.52 g (24.9 mmol) of NEt_3 was added. Hydrolysis and workup led to 1.10 g (97%) of crude **2**. Kugelrohr distillation (50–70°C/0.025 Torr) furnished 0.416 g (36%) of **3**. – Spectroscopical data of **2**: ^1H NMR: δ = 9.43 (d, *J* = 4.2 Hz, 1H, CHO), 3.79 (d, *J* = 2.9 Hz, 1H, 2-H), 1.64 (dd, *J* = 4.2/2.9 Hz, 1H, 1-H), 1.16, 1.11 (2 s, 3H each, 3-Me), 0.76 (s, 9H, *t*BuSi), 0.00, −0.14 (2 s, 6H, Me_2Si). – ^{13}C NMR: δ = 199.3 (d, CHO), 66.1 (d, C-2), 45.0 (d, C-1), 33.7 (s, C-3), 25.5, 17.8, −5.3, −5.4 (q, s, 2 q, *t*$BuMe_2Si$), 18.8, 18.7 (2 s, 3-Me). – Analytical data of **3** are given in Tables 6 and 7.

Oxidation of 2-(tert-Butyldimethylsiloxy)-1-(hydroxymethyl)-2-phenylcyclopropane (**4**): 0.566 g (2.00 mmol) of **4**, dissolved in 2 ml of CH_2Cl_2, was treated with a mixture of 0.281 g (2.21 mmol) of $(COCl)_2$, dissolved in 2 ml of CH_2Cl_2 and 0.378 g (4.84 mmol) of DMSO, according to the general procedure. Addition of 1.19 g (11.8 mmol) of NEt_3 was followed by hydrolysis. 0.535 g (97%) of a mixture of **5** and **6** (90:10) was obtained as crude product. 0.245 g (0.918 mmol) of the crude product was dissolved in 10 ml of CH_2Cl_2 and the solution refluxed for 2 h. The solvent was removed in vacuo, and the residue was purified by chromatography [basic alumina; hexane/ethyl acetate (20:1)]. 0.070 g (27%) of **6** was obtained as a colorless oil. – Spectroscopical data of **5**: ^1H NMR: δ = 8.69 (d, *J* = 6.1 Hz, 1H, CHO), 7.54–7.49, 7.52–7.31 (2 m, 5H, Ph), 2.45 (dt, *J* = 9.3/6.1 Hz, 1H, 1-H), 2.20 (t, *J* = 6.1 Hz, 1H, 3H), 1.78 (dd, *J* = 9.3/6.1 Hz, 1H, 3H), 0.87 (s, 9H, *t*BuSi), 0.05, −0.16 (2 s, 6H, Me_2Si). – ^{13}C NMR: δ = 198.8 (d, CHO), 138.1, 128.9, 128.3 (s, 2 d, Ph, 3rd doublet not detected), 66.9 (s, C-2), 38.9 (d, C-1), 25.4, 17.5, −4.0 (q, s, q, *t*$BuMe_2Si$), 19.9 (t, C-3). – Analytical data of **6**: ^1H- and ^{13}C-NMR data are given in Tables 6 and 7. – IR (film): $\tilde{\nu}$ = 3120–2820 cm^{-1} (CH_{arom}, =CH, −CH), 1620 (C=C), 1250, 950, 830. – $C_{16}H_{24}O_2Si$ (276.5): calcd. C 69.50, H 8.75; found C 68.94, H 8.58.

Oxidation of (Hydroxymethyl)cyclopropanes **7** *and* **11**–**16**: The oxidations were performed as described in the general procedure (Table 1). The crude products were purified by kugelrohr distillation. Analytical data are given in Tables 2–4.

Further analytical data of **8**: MS (EI, 70 eV), *m/z*: 227 (0.3) [M^+ + 1], 226 (1.1) [M^+], 211 (1.7) [M^+ − Me], 169 (38) [M^+ − *t*Bu], 75 (100) [$HOMe_2Si^+$], 73 (75) [Me_3Si^+], 59 (12). – HR MS, $C_{12}H_{22}O_2Si$: calcd. 226.1389; found 226.1389. – $C_8H_{13}O_2Si$: calcd. 169.0685; found 169.0691.

Isomerization of **8** *to 4-(tert-Butyldimethylsiloxy)-2,3-dihydrooxepine* (**9**): A solution of 0.226 g (1.00 mmol) of crude **8** in 10 ml

of CH_2Cl_2 was shaken in a separatory funnel with 5 ml of 2 N HCl, 5 ml of a saturated $NaHCO_3$ solution, and 5 ml of water. The organic layer was dried ($MgSO_4$), and the solvent was removed in vacuo. The crude product (0.208 g, 92%) was filtered through neutral alumina [hexane/ethyl acetate (25:1)], and 0.105 g (46%) of **9** was obtained as a pale yellow oil. – ^{1}H NMR: δ = 6.42 (d, *J* = 7.4 Hz, 1H, 7-H), 5.00 (d, *J* = 8.5 Hz, 1H, 5-H), 4.64 (dd, *J* = 8.5/7.4 Hz, 1H, 6-H), 4.10 (t, *J* = 4.4 Hz, 2H, 2-H), 2.59 (t, *J* = 4.4 Hz, 2H, 3-H), 0.91 (s, 9H, *t*BuSi), 0.14 (s, 6H, Me_2Si). – ^{13}C NMR: δ = 155.0 (s, C-4), 144.7 (d, C-7), 103.5, 100.0 (2 d, C-5,6), 67.3, (t, C-2), 39.2 (t, C-3), 25.5, 17.9, –3.6 (q, s, q, *t*BuMe$_2$Si). – IR (film): $\tilde{\nu}$ = 3620–3140 cm^{-1}, 3040–2780 (=CH, –CH), 1740–1645, 1635 (C=C), 1615, 1470, 1460, 1290, 1250, 1215, 1185, 1140, 885, 830. – MS (EI, 70 eV), *m/z*: 263 (<1), 227 (<1) [M^+], 127 (11), 78 (15), 76 (41), 75 (100) [$HOMe_2Si^+$], 73 (19) [Me_3Si^+], 61 (10), 60 (14), 59 (11), 57 (18), 56 (10), 55 (16), 47 (36), 45 (61), 43 (18), 42 (10), 41 (40), 39 (30). – A correct elemental analysis of this sensitive compound could not be obtained.

2-(tert-Butyldimethylsiloxy)-2,3-dihydro-2-vinylfuran (**10**): According to the general procedure, 0.587 g (2.57 mmol) of **7**, dissolved in 4 ml of CH_2Cl_2, was allowed to react with a mixture of 0.362 g (2.85 mmol) of $(COCl)_2$, dissolved in 6.5 ml of CH_2Cl_2, and 0.482 g (6.17 mmol) of DMSO. Addition of 1.43 g (14.1 mmol) of NEt_3 was

Table 1. Syntheses of 2,5-dihydro-4-siloxyoxepines **8** and **17**–**22** by Swern oxidation of **7** and **11**–**16** according to the general procedure

Starting Compound	g (mmol)	CH_2Cl_2 ml	$(COCl)_2$ g (mmol)	CH_2Cl_2 ml	DMSO g (mmol)	NEt_3 g (mmol)	Product	b.p. °C/Torr[a]	Yield g (%)
7	1.13 (4.95)	5	0.696 (5.48)	12	0.856 (11.0)	2.72 (26.9)	**8**	40/0.01	0.789 (70)
11	0.232 (0.957)	5	0.165 (1.30)	5	0.196 (2.51)	0.590 (5.83)	**17**	40-45/0.01	0.182 (79)
12	0.521 (2.15)	5	0.308 (2.43)	5	0.373 (4.77)	1.18 (11.7)	**18**	40-45/0.01	0.326 (63)
13	0.688 (2.84)	3	0.419 (3.30)	7.5	0.538 (6.88)	1.66 (16.4)	**19**	--	0.593 (87)[b]
14	0.72 (2.97)	6	0.42 (3.31)	6	0.52 (6.65)	1.70 (16.8)	**20**	45-50/0.02	0.353 (49)
15	0.537 (2.00)	2	0.291 (2.30)	5	0.381 (4.87)	1.12 (11.1)	**21**	40-45/0.01	0.371 (70)
16	0.400 (1.56)	2	0.282 (2.22)	5	0.353 (4.52)	0.513 (5.07)	**22**	40-50/0.01	0.176 (44)

[a] Kugelrohr distillation. – [b] Crude product which showed partial isomerization during chromatographical workup.

Table 2. ^{1}H-NMR data (δ values, *J* in Hz) of 2,5-dihydro-4-siloxyoxepines **8** and **17**–**22** (integrals correspond to expected values)

Compound	7-H	3-H	2-H	6-H	5-H	*t*BuSi	Me_2Si	Other Signals
8	6.18 (dt) *J*=7.8, *J*=1.7	5.09 (t) *J*=7.4	4.40 (d) *J*=7.4	4.25 (dt) *J*=7.8, *J*=5.3	2.94 (dd) *J*=5.3, *J*=1.7	0.91 (s)	0.16 (s)[a]	--
17	6.19 (dd) *J*=7.9, *J*=1.7	4.22 (dd) *J*=8.0, *J*=6.5	4.41 (dd) *J*=12.9, *J*=6.5 4.28 (dd) *J*= 12.9, *J*=8.0	4.97 (dd) *J*=7.9, *J*=7.0	2.90 (dquint) *J*=7.0, *J*=1.7	0.91 (s)	0.17 (s) 0.16 (s)	1.23 (d, *J*=7.0, 5-Me)
18	6.15 (dt) *J*=7.7, *J*=1.6	--	4.41 (s)	4.29 (dt) *J*=6.8, *J*=5.5	2.91 (d)[b] *J*=5.5	0.93 (s)	0.11(s) [a]	1.70 (d, *J*=1.1, 3-Me)
19	6.14 (dd) *J*=7.9, *J*=2.2	4.79 (ddd) *J*=6.4, *J*= 2.2, *J*=1.6	4.91 (quint), *J*=6.4	4.23 (dt) *J*=7.9, *J*=2.4	3.54 (dq) *J*=19.5, *J*=2.4 2.25 (dd) *J*=19.5, *J*=7.9[c]	0.89 (s)	0.15 (s) 0.13 (s)	1.26 (d, *J*=6.4, 2-Me)
20	6.15 (q) *J*=1.4	5.08 (t) *J*=7.0	4.29 (d) *J*=7.0	--	2.90 (bs)	0.90 (s)	0.14 (s)[a]	1.52 (dt, *J*=1.4, *J*<1, 6-Me)
21	6.04 (s)	[d]	4.18 (d) *J*=7.1	--	2.74 (s)	0.76 (s)	0.00 (s)[a]	5.63-5.49 (m, 2'-H)[b], 2.38 (d, *J*=6.5, 1'-H)
22	6.01 (q) *J*=1.2	--	4.18 (s)	--	2.77 (s)	0.82 (s)	0.00 (s)[a]	1.56 (d, *J*=1.2, 6-Me), 1.39 (s, 3-Me)

[a] Integral 6H. – [b] Line broadened by long-range coupling (ca. 1 Hz). – [c] Line broadened by long-range coupling with 3-H. – [d] Signal at δ = 4.95–4.84 (m, 3H, 3'-H, 3-H).

Table 3. ^{13}C-NMR data (δ values) of 2,5-dihydro-4-siloxyoxepines **8** and **17**–**22**

Compound	C-4	C-7	C-3	C-6	C-2	C-5	*t*BuSi	Me_2Si	Other Signals
8	160.7 (s)	146.8 (d)	101.9 (d)	98.1 (d)	64.1 (t)	32.2 (t)	25.4 (q) 17.8 (s)	-4.8 (q)[a]	--
17	164.1 (s)	145.5 (d)	105.9 (d)	99.6 (d)	64.0 (t)	38.3 (d)	25.6 (q) 17.9 (s)	-4.5 (q) -4.9 (q)	20.6 (q, 5-Me)
18	152.3 (s)	146.8 (d)	111.3 (s)	98.8 (d)	70.4 (t)	31.8 (t)	25.6 (q) 18.0 (s)	-4.5 (q) -4.8 (q)	15.8 (q, 3-Me)
19	158.0 (s)	146.1 (d)	108.6 (d)	97.6 (d)	70.7 (d)	32.3 (t)	25.5 (q) 17.7 (s)	-4.7 (q) -4.8 (q)	21.4 (q, 2-Me)
20	157.5 (s)	142.4 (d)	103.1 (d)	107.4 (s)	64.3 (t)	38.4 (t)	25.5 (q) 17.9 (s)	-4.7 (q)[a]	21.9 (q, 6-Me)
21	158.4 (s)	143.6 (d)	102.4 (d)	109.2 (s)	64.4 (t)	36.1 (t)	25.5 (q) 17.9 (s)	-4.6 (q)[a]	136.9, 115.9, 40.8 (d, 2t, 6-Allyl)
22	149.2 (s)	142.2 (d)	112.1 (s)	107.8 (s)	70.3 (t)	37.8 (t)	25.7 (q) 18.0 (s)	-4.0 (q)[a]	22.0, 15.7 (2q, 3-Me, 6-Me)

[a] Signal of double intensity.

Table 4. Elemental analyses[a] and IR data ($\tilde{\nu}$ in cm^{-1}, film) of 2,5-dihydro-4-siloxyoxepines **8**, **17**, **18**, **21**, and **22**

Compound	Formula	Molecular weight		C	H	IR data
8	$C_{12}H_{22}O_2Si$	226.4	Calcd. Found	63.66 63.29	9.80 9.86	3600-3080, 3040, 3000-2790 (=CH,-CH), 1650, 1630 (C=C), 1605, 1455, 1360, 1250, 1200, 830
17	$C_{13}H_{24}O_2Si$	240.4	Calcd. Found	64.95 64.65	10.06 10.00	3600-3100, 3030, 2980-2800 (=CH,-CH), 1660, 1645, 1640 (C=C), 1610, 1470, 1455, 1380, 1370, 1250, 830
18	$C_{13}H_{24}O_2Si$	240.4	Calcd. Found	64.95 64.65	10.06 10.06	3600-3100, 3000-2800 (=CH,-CH), 1710, 1650 (C=C), 1460, 1360, 1250, 830
21	$C_{15}H_{26}O_2Si$	266.5	Calcd. Found	67.61 67.28	9.83 9.95	3600-3120, 3070, 2980-2820 (=CH,-CH), 1710, 1660 (C=C), 1465, 1455, 1355, 1250, 830
22	$C_{14}H_{26}O_2Si$	254.5	Calcd. Found	66.07 63.03	10.30 10.27[b]	3600-3100, 3025-2750 (=CH,-CH), 1810-1600 (C=C), 1470, 1460, 1455, 1250, 1200, 835

[a] Compound **20** was analyzed as cycloadduct with 1,1,1-trifluoro-2-nitroso-2-propene[21]. – [b] A correct elemental analysis of this very sensitive compound could not be obtained.

Table 5. Syntheses of 2,3-dihydro-2-siloxyfurans **29**–**32** by Swern oxidation of **25**–**28** according to the general procedure

Starting Compound	g (mmol)	CH_2Cl_2 ml	$(COCl)_2$ g (mmol)	CH_2Cl_2 ml	DMSO g (mmol)	NEt_3 g (mmol)	Product	Yield g (%)
25	0.810 (2.66)	4	0.390 (3.07)	7	0.461[a] (5.90)	1.38 (13.6)	**29**	0.564 (70)[b]
26	0.828 (2.60)	--	0.398 (3.14)	7	0.470 (6.01)	1.42 (14.0)	**30**	0.562 (68)[b]
27	0.175 (0.470)	2	0.085 (0.669)	5	0.107 (1.35)	0.596 (5.89)	**31**	0.106 (61)[c]
28	0.263 (1.12)	1.5	0.16 (0.126)	2	0.18 (2.30)	0.62 (6.13)	**32**	0.267 (93)[d]

[a] Dissolved in 1.5 ml of CH_2Cl_2. – [b] Purification by filtration through basic alumina [hexane/ethyl acetate (20:1) + 1.5% NEt_3)]. – [c] Workup by filtration through neutral alumina [hexane/ethyl acetate (20:1)]. – [d] Crude product, decomposed completely during chromatographical workup (alumina).

followed by hydrolysis giving 0.579 g (100%) of **8** as crude product. The crude product was filtered through basic alumina [hexane/ethyl acetate (25:1)] providing 0.238 g (41%) of **10**. A small amount was purified by kugelrohr distillation (70°C/0.01 Torr) for elemental analysis. – ^{1}H- and ^{13}C-NMR data see Tables 6 and 7. – IR (film): $\tilde{\nu}$ = 3090 cm^{-1}, 2980–2820 (=CH, –CH), 1620 (C=C), 1400, 1250, 1140, 1080, 970, 950, 830. – $C_{12}H_{22}O_2Si$ (226.4): calcd. C 63.66, H 9.79; found C 63.23, H 9.84.

Table 6. ^{1}H-NMR data (δ values, J in Hz) of 2,3-dihydrofurans **3**, **6**, **10**, **23**, **24**, and **29**–**32** (integrals correspond to expected values)

Compound	AMXY system of ring protons δ_A(5-H)	δ_M(4-H)	δ_X(3-H)	δ_Y(3-H)	$J_{AM}=J_{AX}=J_{AY}=J_{MX}=J_{MY}$	J_{XY}	*t*BuSi	Me_2Si	Other Signals
3	6.14	4.79	--	--	2.5		0.86 (s)	0.10 (s) 0.09 (s)	5.23 (s, 2-H), 1.04, 1.02 (2s, 3-Me)
6	6.49	5.04	2.91	2.83	2.5	16.5	0.97 (s)	0.11 (s) -0.03 (s)	7.55-7.50, 7.42-7.28 (2m Ph)
10	6.28	4.91	2.71	2.58	2.5	16.4	0.90 (s)	0.12 (s) 0.09 (s)	6.00, 5.39, 5.11 (ABX-System, J_{AX}= 17.1, J_{BX}=10.5, J_{AB}=1.5, H_2C=CH)
23	6.26	4.88	2.66	2.51	2.5	16.4	0.85 (s)	0.11 (s) 0.10 (s)	5.14, 4.77 ($2m_c$, 2'-H), 1.73 (d, J=1.1, 1'-Me)
24	6.24	4.88	2.68	2.54	2.5	16.4	0.88 (s)	0.10 (s) 0.07 (s)	5.83 (dq, J=15.3, J=6.5, 2'-H), 5.63 (dq, J=15.3, J=1.5, 1'-H), 1.70 (dd, J=6.5, J=1.5, 3'-H)
29	6.35	4.98	2.83	2.69	2.5	16.4	0.96 (s)	0.16 (s) 0.14 (s)	7.43-7.26 (m, Ph), 6.79, 6.39 (2d, J=15.9, CH=CH)
30	6.12[a]	--	2.80[b]	2.63[b]	--	16.2	0.99 (s)	0.19 (s) 0.16 (s)	7.47-7.29 (m, Ph), 6.79, 6.39 (2d, J= 15.9, -CH=CH-), 1.73 (d, J=1.2, 4-Me)
31	6.35	4.99	2.82	2.70	2.5	16.5	0.94 (s)	0.14 (s) 0.13 (s)	7.64-7.56, 7.54-7.48 (2m, C_6H_4), 6.75, 6.44 (2d, J=15.9, CH=CH)
32	6.22	4.88	2.68	2.58	2.5	16.5	[c]	[d]	6.69, 4.94 (2d, J=12.5, 1'-H, 2'-H), 3.51 (s, OMe)

[a] Multiplet. – [b] Line broadened by long-range coupling. – [c] Signals at δ = 0.90–0.78 (m, 19H, *t*BuSi and impurities). – [d] Signals at δ = 0.01–0.00 (m, 9H, Me_2Si and impurities).

Table 7. ^{13}C-NMR data (δ values, J in Hz) of 2,3-dihydro-2-siloxyfurans **3**, **6**, **10**, **23**, **24**, and **29**–**32**

Compound	C-5	C-2	C-4	C-3	*t*BuSi	Me_2Si	Other Signals
3	141.3 (d)	111.8 (d)	106.7 (d)	45.6 (t)	25.3 (q) 17.9 (s)	-3.7 (q) -5.4 (q)	27.2, 20.8 (2q, 3-Me)
6	143.5 (d)	109.2 (s)	99.4 (d)	47.2 (s)	26.0 (q) 18.1 (s)	-3.3 (q) -3.4 (q)	145.6, 127.7, 127.5, 125.0 (s, 3d, Ph)
10	143.2 (d)	108.0 (s)	99.0 (d)	43.9 (t)	25.8 (q) 18.0 (s)	-3.2 (q) -3.4 (q)	140.1, 113.5 (d, t, H_2C=CH-)
23	143.2 (d)	109.4 (s)	98.9 (d)	43.3 (t)	25.7 (q)[a]	-3.6 (q) -4.2 (q)	110.2 (t, C-2'), 17.9 (q, 1'-Me)
24	142.9 (d)	107.8 (s)	98.8 (d)	43.9 (t)	25.6 (q) 18.7 (s)	-3.4 (q) -3.6 (q)	133.4 (d, C-1'), 124.5 (d, C-2'), 11.0 (q, 2'-Me)
29	143.1 (d)	108.1 (s)	99.2 (d)	44.4 (t)	25.8 (q) 17.9 (s)	-3.2 (q) -3.4 (q)	136.4, 131.4, 128.7, 128.5, 127.5, 126.5 (s, 5d, Ph-CH=CH)
30	137.2 (d)	[b]	[b]	48.9 (t)	25.6 (q) 17.8 (s)	-3.3 (q) -3.6 (q)	136.2, 131.6, 128.3, 127.5, 126.5 (s, 5d, Ph-CH=CH), 11.0 (q, 4-Me)
31	143.3 (d)	107.9 (s)	99.5 (d)	44.5 (t)	25.9 (q) 18.5 (s)	-3.3 (q) -3.6 (q)	140.1, 134.1, 127.5, 127.0, 125.6 (s, 4d, C_6H_4-CH=CH), 124.3 (q, J_{CF}=272, *p*-CF_3)[c]
32	142.9 (d)	108.0 (s)	99.2 (d)	45.8 (t)	25.6 (q) 18.3 (s)	-3.4 (q) -3.8 (q)	147.3, 106.9 (2d, C-2', C-1'), 55.8 (q, OMe)

[a] The signal of quaternary C atom was not detected. – [b] Signals at δ = 108.9 (s) and 107.5 (s), unambiguous assignment not possible. – [c] Signal of the *p*-C atom was not detected.

Isomerization of **19** *to 2(tert-Butyldimethylsiloxy)-2,3-dihydro-2-(1-propenyl)furan* (**24**): 0.312 g (1.30 mmol) of crude **19** (Table 1, entry 4) was filtrered through Florisil [hexane/ethyl acetate (25:1) + 1.5 vol-% NEt_3] and led to 0.196 g (63%) of **24**. – ^{1}H- and ^{13}C-NMR data are given in Tables 6 and 7. – IR (film): $\tilde{\nu}$ = 3090 cm^{-1}, 3025–2800 (=CH, –CH), 1670, 1615 (C=C), 1465, 1455, 1245, 950, 830. – $C_{13}H_{24}O_2Si$ (240.4): calcd. C 64.95, H 10.06; found C 64.27, H 10.05.

Oxidation of (Hydroxymethyl)cyclopropanes **25–28**: The oxidation was performed according to the general procedure (Table 5). – ^{1}H- and ^{13}C-NMR data are given in Tables 6 und 7.

Further analytical data: **29**: IR (film): $\tilde{\nu}$ = 3100–2800 cm^{-1} (CH_{arom}, =CH, –CH), 1615 (C=C), 1245, 995, 830. – $C_{18}H_{26}O_2Si$ (302.5): calcd. C 71.47, H 8.66; found C 71.66, H 8.66. – **30**: IR (film): $\tilde{\nu}$ = 3100–2760 cm^{-1} (CH_{arom}, =CH, –CH), 1670 (C=C), 1250, 1130, 890. – $C_{19}H_{28}O_2Si$ (316.5): calcd. C 72.10, H 8.91; found C 71.86, H 8.89. – **31**: IR (film): $\tilde{\nu}$ = 2980–2820 cm^{-1} (=CH, –CH), 1615 (C=C), 1460–1360, 1325, 1250, 1165, 1130 (CF_3), 835. – $C_{19}H_{25}F_3O_2Si$ (370.5): calcd. C 61.60, H 6.80; found C 62.44, H 7.41; a better elemental analysis could not be obtained.

2-(2-Phenylvinyl)furan (**33**): According to the general procedure, a mixture of 0.709 g (5.59 mmol) of $(COCl)_2$, dissolved in 12 ml of CH_2Cl_2 and 0.899 g (11.5 mmol) of DMSO, was allowed to react with a solution of 1.46 g (4.84 mmol) of **25** in 7 ml of CH_2Cl_2. After addition of **25** the mixture was stirred for 30 min. Then 3.5 ml of NEt_3 was added, and the mixture was stirred for further 1.5 h at –60°C before the cooling bath was removed and the mixture was stirred at room temp. for 1 h. Hydrolysis (25 ml of water) was followed by separation of the layers, and the organic phase was washed twice with 50 ml of 2 N HCl, 50 ml of a $NaHCO_3$ solution (5% by weight), and 50 ml of water. After drying ($MgSO_4$) the solvent was removed in vacuo, and 1.22 g (83%) of crude product was obtained. Chromatography [neutral alumina; hexane/ethyl acetate (20:1)] afforded 0.509 g (62%) of **33** as a pale yellow solid (m.p. 47–50°C), containing small amounts of siloxane. – ^{1}H NMR: δ = 7.48–7.03 (m, 6H, Ph, 5-H), 6.94, 6.79 (2 d, J = 16.3 Hz, 1H each, CH=CH), 6.31, 6.24 (2 m, 1H each, 3,4-H). – ^{13}C NMR: δ = 153.1 (s, C-2), 141.9 (d, C-5), 136.9 (s, *i*-C, Ph), 128.5, 126.2 (2 d, *o/m*-C, Ph), 127.4, 127.0, 116.4, 111.5, 108.4 (5 d, *p*-C, Ph, CH=CH, C-3,4). For further characterization see ref.[23].

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