A General Synthesis of (*Z*)-1,2-Ethenediol Derivatives

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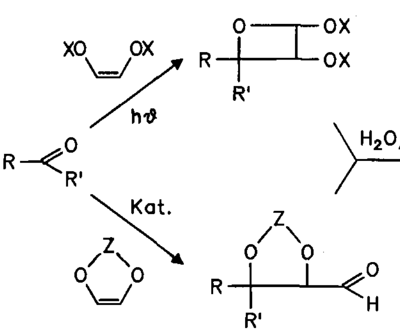
Received September 14, 1991

Key Words: Ethenes, (Z)-1,2-disubstituted / retro-Diels-Alder synthesis / 1,3,6,8-Tetraoxa-2,7-disilacyclodeca-4,9-diene, (Z,Z)-2,2,7,7-tetraalkyl-, preparation of / 1,3,2-Dioxasiloles, dimerization of

By retro-Diels-Alder reaction of suitably substituted 9,10-dihydro-9,10-ethanoanthracene-*cis*-11,12-diol derivatives (**4**, **6**, **8**, **10**, **12**, **14**) a number of known and unknown (Z)-1,2-disubstituted ethenes (**5**, **7**, **9**, **11**, **13**, **14**) have been prepared in high yield, including derivatives with two different substituents. In contrast to this, attempts to prepare 1,3,2-dioxasiloles bearing only substituents on the silicon atom gave dimers containing the ten-membered ring system (Z,Z)-2,2,7,7-tetraalkyl-1,3,6,8-tetraoxa-2,7-disilacyclodeca-4,9-diene (**19b**, **21b**, **23b**, **25b**). Again these compounds are formed diastereoselectively with respect to the double bonds.

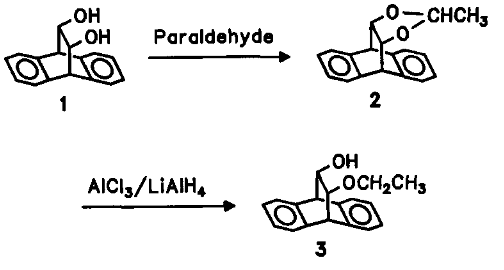
(*Z*)-Ethenediol derivatives are important building blocks in the synthesis of both low-molecular weight compounds and macromolecules. In photoaldol reactions (Paterno-Büchi reaction) or in the aldol reaction with aldehydes or ketones, ethenediol derivatives are used as synthetic equivalents of the glycolaldehyde anion $[^{-}CH(OH)-CHO]$[1–3] (see Scheme 1). For example, it is possible to start from D- or L-glyceraldehyde and synthesize the corresponding pentoses by a two-carbon atom extension[2].

Scheme 1. Preparative applications of (*Z*)-1,2-disubstituted ethenes



In polymer chemistry, (*Z*)-1,2-ethenediol derivatives may be used to obtain a macromolecule carrying on each main chain carbon atom an oxygen functional group. Usually, this results in hydrophilic or water soluble polymers[4–7]. The stereochemistry of the aldol reaction is controlled by using ethenediol derivatives of (*Z*) configuration; in polymer chemistry only the (*Z*) derivative polymerizes readily[5,8].

Up to now there has been no general route to diastereomerically pure cyclic or acyclic (*Z*) 1,2-ethenediol derivatives. The preparation of (*Z*)-ethenediol, the parent compound, was first described in 1982 by Ripoll and Lasne[9] by a retro-Diels-Alder reaction of the diol **1**. By a similar route, we were able to synthesize 1,3,2-dioxaboroles **17**[1,2] substituted only at the 2-position. In virtue of these experiments, we wanted to work out a more general synthesis of both known and unknown (*Z*)-1,2-ethenediol derivatives.



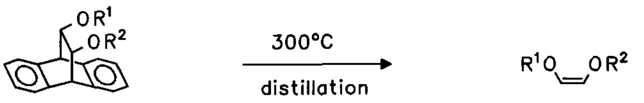
Results and Discussion

The starting material for our syntheses is the known diol **1**[10], obtained by Diels-Alder reaction of vinylene carbonate with anthracene, followed by hydrolysis of the carbonate ester group. An improved synthesis of vinylene carbonate is described here (see Experimental), allowing a simple and efficient route to diol **1**. Silylation or acylation gives the disilyl compound **4** or the diacetate **6**. Thermolysis of **4** or **6** at 300 °C with removal of the product by distillation yields the (*Z*)-1,2-ethenediol disilyl ether **5** and the diacetate **7**, resp., in diastereomerically pure form. The disilyl compound **5** is obtained in an overall yield of 71% by starting from vinylene carbonate. This method is superior to the one-step procedure which affords only 13%[11] or 39%[3] yields. (*Z*)-1,2-Vinylene diacetate (**7**) has already been obtained in a somewhat higher yield but not in diastereomerically pure form[12].

Starting from diol **1**, we have not only obtained symmetrical but also unsymmetrical (*Z*)-1,2-ethenediol derivatives. The reaction of **1** with paraldehyde furnishes acetal **2** in nearly quantitative yield. Reductive ring opening[13] of **2** by $AlCl_3/LiAlH_4$ yields the monoether **3** of diol **1** in an overall yield of 94% with respect to **1**. Silylation with trimethylsilyl chloride, dimethylphenylsilyl chloride, or *tert*-butyldimethylsilyl chloride yielded the mixed diethers **10**, **12**, and **14**, respectively. It should be noted that the unsymmetrically substituted derivatives of diol **1** (**3**, **8**, **10**, **12**, **14**) thus become chiral and are obtained as racemic mixtures. In the ^{1}H-NMR spectrum of **14**, the two diastereotopic CH_3 groups at Si of the *tert*-butyldimethylsilyl group give rise to two signals.

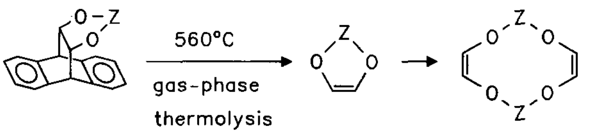
Chem. Ber. **1992**, *125*, 473–477 © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1992 0009–2940/92/0202–0473 $ 3.50+.25/0

Thermolysis of compounds **10**, **12**, and **14** at 300 °C produces the (*Z*)-1,2-ethenediol derivatives **11**, **13**, and **15** in high yield. These new compounds are obtained chemically and diastereomerically pure. Compounds **11**, **13**, **15** represent interesting (*Z*)-1,2-ethenediol derivatives since they bear two very different oxygen functionalities, one of which can be easily hydrolyzed to a hydroxyl group. They may also show interesting applications in the aldol reaction. Recently, the cationic polymerization of (*Z*)-1-acetoxy-2-ethoxyethene (**9**) (which is obtained by thermolysis of **8**) has been reported[14].



	R^1	R^2	
4	$Si(CH_3)_3$	$Si(CH_3)_3$	5
6	$COCH_3$	$COCH_3$	7
8	$COCH_3$	C_2H_5	9
10	C_2H_5	$Si(CH_3)_3$	11
12	C_2H_5	$Si(CH_3)_2C_6H_5$	13
14	C_2H_5	$Si(CH_3)_2C(CH_3)_3$	15

The cyclic (*Z*)-1,2-ethenediol derivative **17** has been obtained from the phenylboronic ester **16**[1,2]. It has been of interest to see whether 1,3,2-dioxasiloles can be obtained by the same method. The first problem is to prepare the corresponding starting compounds **18**, **20**, **22**, **24**. Silicon compounds with two reactive groups are prone to oligomerization with diols[15,16]. In fact, the reaction of diol **1** with dialkyldichlorosilane in the presence of triethylamine yielded predominantly oligomeric and polymeric silicones. Careful optimization of the reaction conditions considerably improves this reaction, and yields of up to 71% for **18**, **20**, **22**, **24** can finally be obtained. These high yields are somewhat surprising. The main advantage of our procedure is the use of sodium hydride as a base, affording a dialcoholate which is insoluble in tetrahydrofuran. The reaction of the dichlorosilane must take place at the liquid-solid phase boundary, and this is assumed to facilitate an intramolecular rather than an intermolecular reaction.



	Z		
16	$B-C_6H_5$	17	–
18	$Si(CH_3)_2$	19a	19b
20	$Si(C_2H_5)_2$	21a	21b
22	$Si(C_2H_5)CH_3$	23a	23b
24	$Si(CH_3)C_6H_5$	25a	25b

Derivatives are obtained with two identical substituents at the silicon atom ($R = R' = CH_3$, **18**, and $R = R' = C_2H_5$, **20**) and with two different ones ($R = CH_3$, $R' = C_2H_5$, **22**, and $R = CH_3$, $R' = C_6H_5$, **24**). The two substituents at the silicon atom can be oriented in an *endo*- or *exo*-position with regard to the dihydroanthracene system. It is possible to distinguish between these two positions by ^{1}H-NMR spectroscopy. For example, in **18** the two methyl groups show absorptions at $\delta = -0.8$ (*endo*) and $+0.07$ (*exo*). This means that the *endo*-substituent shows a high-field shift whereas the signal of the *exo*-substituent is in the usual position. More interestingly, for **22** and **24** containing an unsymmetrically substituted silicon, one should expect two diastereoisomers. Due to the anisotropic effect of the dihydroanthracene ring system, the assignment of the signals to *endo*- and *exo*-isomers is possible, and the diastereomeric excess can be determined. In both cases the diastereoisomer in which the more bulky substituent is in the *exo*-position is preferred. For the 2-ethyl-2-methyl derivative **22**, the excess is 8%; for the 2-methyl-2-phenyl derivative **24**, it is 65% in favor of the phenyl substituent in the *exo*-position.

Compounds **18**, **20**, **22**, **24** do not undergo thermolysis and distillation at 300 °C, i.e. under the conditions used to produce **4**, **6**, **10**, **12**, and **14**. Rather, like the boron derivative **16**[1,2], a gas-phase thermolysis at 560 °C/10^{-2} mbar is necessary for a successful retro-Diels-Alder reaction. The cyclic ethenediol derivatives **17** and **19**, **21**, **23**, **24** are also much more thermally stable. The acyclic ethenediol derivatives decompose at the higher temperatures used in gas-phase thermolysis.

The thermolyses of **18**, **20**, **22**, and **24** have been expected to yield the 4,5-unsubstituted 2,2-dialkyl(aryl)-1,3,2-dioxasiloles **19a**, **21a**, **23a**, **25a**, which have not been described before. 1,3,2-Dioxasiloles bearing substituents in the 4- and 5-position are reported to be highly reactive[15,17]. In contrast, compounds **19**, **21**, **23**, and **25** are relatively stable even in air. The reason for this stability may be that **19**, **21**, **23**, and **25** are, in fact, dimeric. After their preparation in the gas phase they are most probably monomeric, but on condensation in the trap at −196 °C or on warming to room temperature they dimerize. Thus, by means of this synthesis, the new 2,7-disubstituted 1,3,6,8-tetraoxa-2,7-disilacyclodeca-4,9-dienes **19b**, **21b**, **23b**, **25b** are obtained. The dimeric nature of the compounds has been detected by vapor pressure osmometry and mass spectroscopy. Mass spectra, in addition to those of the dimers show the expected peaks for the cation of the five-membered rings **19a**, **21a**, **23a**, and **25a**. It has not been possible, by analogy with experiments performed by Meyer et al.[18], to obtain the monomeric species by distillation or heating of the dimers, leading to the conclusion that the monomeric species **19a**, **21a**, **23a**, and **25a** are highly reactive and spontaneously dimerize at or below room temperature.

The signals for the vinyl protons of the dimers **19b**, **21b**, **23b**, and **25b** appear in the ^{1}H-NMR spectra at $\delta = 5.67-5.73$ as a singlet. A comparison of these shifts with those of the vinyl protons of (*Z*)-1,2-bis(trimethylsilyloxy)ethene ($\delta = 5.40$) and (*E*)-1,2-bis(trimethylsilyloxy)ethene (6.53)[3] reveals that the configuration of both double bonds in the dimers is still (*Z*). Compounds **19** and **21**, bearing two identical substituents in the 2- and 7-position, are diastereomerically pure (*Z*,*Z*)-2,2,7,7-tetraalkyl-1,3,6,8-tetraoxa-2,7-disilacyclo-4,9-dienes. For the dimers of the unsymmetrically substituted monomers **23a** and **25a**, two diastereoisomers are expected since the two methyl groups in **23b** and **25b** at C-2 and C-7 can have a *cis*- or a *trans*-arrangement with respect to each other, depending on the transition state of the dimerization. In Figure 1 possible transition states of the dimerization are shown. In the case of **21**, both diastereoisomers are formed in nearly equal amounts, and in the case of **23**, an excess of 19% is observed. We have not attempted to determine which isomer is formed in excess.

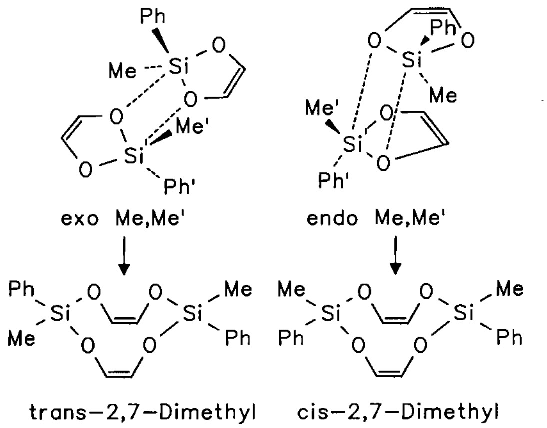


Figure 1. Possible transition states of the dimerization of **25a**

In conclusion, it has been possible to prepare diastereoselectively a variety of cyclic and acyclic (*Z*)-1,2-ethenediol derivatives by using the starting diol **1**. The known acyclic disubstituted (*Z*)-1,2-ethenediol derivatives **5** and **7** are prepared in higher yields. For the first time, (*Z*)-1,2-ethenediol derivatives **11**, **13**, and **15**, bearing two different substituents have been synthesized. Attempts to prepare cyclic 1,3,2-dioxasiloles **19a**, **21a**, **23a**, and **25a** have proved abortive since they dimerize to the corresponding ten-membered ring systems **19b**, **21b**, **23b**, and **25b**. These compounds can be obtained diastereoselectively with respect to the double bonds.

This investigation was supported by grants from *Deutsche Forschungsgemeinschaft* and *Fonds der Chemischen Industrie*.

Experimental

Elemental analyses: Mikroanalytisches Laboratorium der Naturwissenschaftlichen Fakultät der Universität Düsseldorf. — ^{1}H and ^{13}C NMR: Varian EM 390 and VXR 300. — Melting points: Büchi 510 apparatus. — MS: Varian MAT CH-50 and MAT 311 A. — IR: Perkin-Elmer 297. — Vapor pressure osmometry: in THF, apparatus from the Knauer Company.

Vinylene Carbonate: 80 g (0.91 mol) of ethylene carbonate and 122.9 g (0.91 mol) of sulfuryl chloride were heated to 80°C in 500 ml of dry CCl_4 with irradiation of a 500-W UV lamp. The vigorous reaction could be controlled by regulating the intensity of irradiation. SO_2 and HCl are formed and absorbed in aqueous NaOH. After 2—3 h the reaction was stopped and the mixture cooled to 20°C. The resulting layers were separated, and the lower CCl_4 layer was used again for the next experiment. The upper layer containing most of the reaction product was distilled, providing 70—75% monochloroethylene carbonate besides ethylene and dichloroethylene carbonate (^{1}H-NMR analysis). This mixture was directly used for elimination of HCl according to the method of Addor[19]. Fractional distillation of the mixture (b.p. 50°C/20 mbar) yielded 39.1 g of pure vinylene carbonate (50% after the two steps).

9,10-Dihydro-9,10-ethanoanthracene-cis-11,12-diol (**1**) was prepared as described by Patton[10].

9,10-Dihydro-cis-11,12-bis(trimethylsilyloxy)-9,10-ethanoanthracene (**4**): To a solution of **1** (15 g, 63 mmol) and triethylamine (38 g, 0.38 mol) in dry THF (300 ml) chlorotrimethylsilane (41 g, 0.38 mol) was added dropwise. The mixture was kept at room temp. for 60 h. After removal of the precipitate by filtration and evaporation of the solvent from the filtrate, the resulting residue was dissolved in hexane. Another precipitate was removed and the solution concentrated. The residue was purified by sublimation (80—100°C, 0.1 mbar). Yield 20.0 g (83%), m.p. 87°C. — ^{1}H NMR ($CDCl_3$): δ = 0.1 (s, 18H, $SiCH_3$), 4.0—4.2 (m, 4H, CHO, —CH—), 7.0—7.33 (m, 8H, aromatic H). — MS (70 eV): m/z = 367 [M — 15].

$C_{22}H_{30}O_2Si$ (382.7) Calcd. C 69.05 H 7.90
Found C 69.74 H 7.88

cis-11,12-Diacetoxy-9,10-dihydro-9,10-ethanoanthracene (**6**): To a mixture of **1** (23.8 g, 0.1 mol) in acetic anhydride (60 ml) was added 5 drops of conc. H_2SO_4, and the mixture was refluxed for 4 h. After the usual workup, the substance was crystallized from petroleum ether (100—140°C). Yield 19.0 g (59%), m.p. 153°C. — ^{1}H NMR ($CDCl_3$): δ = 1.87 (s, 6H, $COCH_3$), 4.40—4.46 (m, 2H, —CH—), 5.03—5.16 (m, 2H, HCOAc), 7.0—7.36 (m, 8H, aromatic H). — MS (70 eV): m/z = 322 [M^+].

(±)-cis-12-Ethoxy-9,10-dihydro-9,10-ethanoanthracene-11-ol (**3**): A mixture of **1** (50 g, 0.21 mol), paraldehyde (40 g, 0.3 mol), and 4-toluenesulfonic acid (1.8 g) in toluene (1 l) was heated for 5 h with azeotropic removal of water. After the usual workup, 1,3-dioxolane **2** was crystallized from petroleum ether (100—140°C), yield 53.8 g (97%), m.p. 172°C. Under these conditions only the *endo* isomer was obtained [^{1}H NMR ($CDCl_3$): δ = 0.7 (d, 3H, CH_3), 5.0 (q, 1H, OCHO *exo*)]. After prolonged heating with addition of water the *exo*-isomer was formed [^{1}H NMR ($CDCl_3$): δ = 1.0 (d, 3H, CH_3), 3.73 (q, 1H, OCHO *endo*)]. For the preparation of **3**, the crude reaction product of **2** (39.6 g, 0.15 mol) was dissolved in CH_2Cl_2/diethyl ether (580 ml, 1:1, v/v). $LiAlH_4$ (20 g, 0.53 mol) and a solution of $AlCl_3$ (80 g, 0.6 mol) in dry diethyl ether (230 ml) were added one after the other during 20 min. The mixture was heated for 6 h under reflux and kept at room temp. overnight. After successive addition of ethyl acetate (100 ml), methanol (100 ml), and water (500 ml), the organic phase was separated and the aqueous solution extracted twice with $CHCl_3$. After drying of the combined organic extracts with Na_2SO_4 the solvent was removed in vacuo. The product obtained could be used directly for further reactions. Yield 52.6 g (94%) (with respect to **1**), m.p. 136°C. — ^{1}H NMR ($CDCl_3$): δ = 1.1 (t, J = 7 Hz, 3H, OCH_2CH_3), 2.83 (s, 1H, OH), 3.33—4.50 (m, 6H, OCH_2, OCH, —CH—), 7.0—7.4 (m, 8H, aromatic H). — IR (KBr): $\tilde{\nu}$ = 3470 cm^{-1} (OH). — MS (70 eV): m/z = 221 [M — OEt].

$C_{18}H_{18}O_2$ (266.3) Calcd. C 81.17 H 6.81
Found C 81.21 H 6.87

(±)-cis-11-Ethoxy-9,10-dihydro-12-(trimethylsilyloxy)-9,10-ethanoanthracene (**10**): Compound **3** was silylated as described for **4**. Purification by sublimation (110°C/0.4 mbar). Yield 20.1 g (93%),

m.p. 120°C. – ^1H NMR ($CDCl_3$): δ = 0.13 (s, 9H, $SiCH_3$), 1.13 (t, *J* = 7.5 Hz, 3H, OCH_2CH_3), 3.43–3.77 (m, 3H, $HC-O-CH_2CH_3$), 4.10–4.23 (m, 2H, HCOSi, –CH–), 4.43 (d, *J* = 3 Hz, 1H, –CH–), 6.94–7.33 (m, 8H, aromatic H). – MS (70 eV): *m/z* = 323 (M – CH_3).

$C_{21}H_{26}O_2Si$ (338.5) Calcd. C 74.51 H 7.74
Found C 74.68 H 7.95

(±)-cis-11-(Dimethylphenylsilyloxy)-12-ethoxy-9,10-dihydro-9,10-ethanoanthracene (**12**): The starting compound **3** was silylated with dimethylphenylsilyl chloride in the same manner as in the synthesis of **6**. The product was purified by recrystallization from petroleum ether (40–60°C) at 4°C. Yield 30.8 g (77%), m.p. 120°C. – ^1H NMR ($CDCl_3$): δ = 0.13 (s, 6H, $SiCH_3$), 0.83 (t, *J* = 6 Hz, 3H, CH_2CH_3), 3.1–3.53 (m, 3H, $HC-O-CH_2$), 3.8–4.3 (m, 2H, –CH–, HCOSi), 4.16 (d, *J* = 3 Hz, 1H, –CH–), 6.67–7.4 (m, 13H, aromatic H). – MS (70 eV): *m/z* = 400 [M^+].

$C_{26}H_{28}O_2Si$ (400.6) Calcd. C 77.96 H 7.05
Found C 78.12 H 7.18

(±)-cis-11-(tert-Butyldimethylsilyloxy)-12-ethoxy-9,10-dihydro-9,10-ethanoanthracene (**14**): A solution of **3** (10 g, 38 mmol) in dry THF (10 ml) was treated under nitrogen with sodium hydride (2 g, 80%) at room temp. for 4 h. *tert*-Butyldimethylsilyl chloride (6.8 g, 45 mmol), dissolved in dry THF (50 ml), was added dropwise, and the reaction mixture was stirred at room temp. for 50 h. After the usual workup, 8.4 g **14** was obtained (58%), m.p. 76°C [petroleum ether (100–140°C), cooled to 4°C]. – ^1H NMR ($CDCl_3$): δ = –0.05 (s, 3H, $SiCH_3$), 0.05 (s, 3H, $SiCH_3$), 0.77 [s, 9H, $SiC(CH_3)_3$], 1.03 (t, *J* = 7.5 Hz, 3H, CH_2CH_3), 3.27–3.70 (m, 3H, $HC-O-CH_2$), 4.00–4.20 (m, 2H, –CH–, HCOSi), 4.33 (d, *J* = 3 Hz, 1H, –CH–), 6.90–7.30 (m, 8H, aromatic H). – MS (70 eV): *m/z* = 380 [M^+], 365 [M – CH_3], 323 [M – $C(CH_3)_3$].

$C_{24}H_{32}O_2Si$ (380.6) Calcd. C 75.74 H 8.47
Found C 75.63 H 8.51

4,5-(9,10-Dihydro-9,10-anthracenylene)-2,2-dimethyl-1,3,2-dioxasilolane (**18**): To a stirred suspension of NaH (3.1 g, 0.1 mol, 80%) in dry THF (400 ml) was added dropwise **1** (10.5 g, 44 mmol) and the mixture heated to 50–60°C under nitrogen for 4 h. The mixture was allowed to cool, and a solution of dichlorodimethylsilane (80 mmol) in dry THF (100 ml) was added at room temp. during 2 h. The mixture was kept overnight and then filtered. After evaporation of the solvent, hexane (1 l) was added to the residue, and the solution again filtered to remove polymeric material. After evaporation of the hexane from the filtrate the obtained material was purified by sublimation (60–80°C, 0.08 mbar). Yield 9.2 g (71%), m.p. 110°C. – ^1H NMR ($CDCl_3$): δ = –0.8 (s, 3H, $SiCH_3$ *endo*), 0.07 (s, 3H, $SiCH_3$ *exo*), 4.43 (s, 4H, –CH–, CHO), 6.96–7.37 (m, 8H, aromatic H). – MS (70 eV): *m/z* = 294 [M^+].

$C_{18}H_{18}O_2Si$ (294.3) Calcd. C 73.43 H 6.16
Found C 73.37 H 6.30

4,5-(9,10-Dihydro-9,10-anthracenylen)-2,2-diethyl-1,3,2-dioxasilolane (**20**) was prepared as described for **18** by using **1** and dichlorodiethylsilane. Yield 8.5 g (60%). – ^1H NMR ($CDCl_3$): δ = 0.4–0.8 (m, 10H, CH_2CH_3), 4.4 (s, 4H, CHO, –CH–), 6.93–7.33 (m, 8H, aromatic H). Compound **20** gave no satisfactory elemental analysis.

4,5-(9,10-Dihydro-9,10-anthracenylen)-2-ethyl-2-methyl-1,3,2-dioxasilolane (**22**) was prepared as described for **18** by using **1** and dichloroethylmethylsilane. Purification by sublimation at 160°C/0.08 mbar. Yield 6.0 g (44%) of a diastereomeric mixture of 54% *exo*-ethyl and 46% *endo*-ethyl isomer (^1H-NMR analysis). – ^1H NMR ($CDCl_3$): δ = –0.83 (s, 3H, $SiCH_3$ *endo*), –0.5 (q, 2H, $SiCH_2$ *endo*), 0.1 (s, 3H, $SiCH_3$ *exo*), 0.37–1.83 (m, 5H, $SiCH_2CH_3$ *exo*), 0.63 (t, 3H, $SiCH_2CH_3$ *endo*), 4.47 (s, 8H, CHO, –CH–), 6.93–7.43 (m, 16H, aromatic H). – MS (70 eV): *m/z* = 308 [M^+].

$C_{19}H_{20}O_2Si$ (308.5) Calcd. C 73.98 H 6.54
Found C 74.29 H 6.46

4,5-(9,10-Dihydro-9,10-anthracenylen)-2-methyl-2-phenyl-1,3,2-dioxasilolane (**24**) was prepared as described for **18** by using **1** and dichloromethylphenylsilane. Purification by sublimation (140°C, 0.08 mbar). Yield 10.0 g (64%) (de = 65%, *exo*-phenyl compound in excess). – ^1H NMR ($CDCl_3$): δ = –0.5 (s, 3H, $SiCH_3$ *endo*), 0.37 (s, 3H, $SiCH_3$ *exo*), 4.47–4.70 (m, 8H, CHO, –CH–), 6.50–6.63 and 7.00–7.53 (m, 13H, aromatic H, *endo* phenyl), 7.00–7.53 (m, 13H, aromatic H, *exo* phenyl). – MS (70 eV): m/z = 356 [M^+].

$C_{23}H_{20}O_2Si$ (356.5) Calcd. C 77.49 H 5.65
Found C 77.22 H 5.57

General Procedure for the Retro-Diels-Alder Reaction Using Distillation[20]: About 15 mmol of compounds **4**, **6**, **10**, **12**, and **14** were heated in a distillation apparatus to ca. 300°C. At this temperature the products **5**, **7**, **11**, **13**, and **15** distilled off with small amounts of anthracene, which can be removed by filtration. The liquid products were, with the exception of **13**, directly analytically pure.

(Z)-1,2-Bis(trimethylsilyloxy)ethene (**5**): Yield starting from **4**, 3.0 g (97%). – ^1H NMR ($CDCl_3$): δ = 0.17 (s, 18H, $SiCH_3$), 5.46 (s, 2H, =CH) in accordance with the literature values[3,11].

(Z)-1,2-Diacetoxyethene (**7**): Yield starting from **6**, 1.0 g (53%). – ^1H NMR ($CDCl_3$): δ = 2.17 (s, 6H, $COCH_3$), 6.80 (s, 2H, =CH) in accordance with the literature values[12].

(Z)-1-Ethoxy-2-(trimethylsilyloxy)ethene (**11**): Yield starting from **10**, 2.15 g (89%). – ^1H NMR ($CDCl_3$): δ = 0.20 (s, 9H, $SiCH_3$), 1.27 (t, *J* = 7.1 Hz, 3H, CH_2CH_3), 3.80 (q, *J* = 7.1 Hz, 2H, CH_2CH_3), 3.58 (d, *J* = 3.4 Hz, 1H, HCOEt), 5.45 (d, *J* = 3.4 Hz, 1H, HCOSi). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = –0.41 (3 C, $SiCH_3$), 15.15 (1 C, CH_2CH_3), 68.00 (1 C, CH_2), 121.64 (1 C, =COSi), 131.21 (1 C, =COEt). – MS (70 eV): *m/z* = 160 [M^+].

$C_{17}H_{16}O_2Si$ (160.3) Calcd. C 52.45 H 10.06
Found C 52.07 H 9.97

(Z)-1-(Dimethylphenylsilyloxy)-2-ethoxyethene (**13**): Yield starting from **12**, 1.2 g (36%). In this case the product was purified by distillation. B.p. 80°C/5 mbar. – ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.46 (s, 6H, $SiCH_3$), 1.24 (t, *J* = 7.1 Hz, 3H, CH_2CH_3), 3.76 (q, *J* = 7.1 Hz, 2H, $-CH_2-$), 5.35 (d, *J* = 3.4 Hz, 1H, HCOEt), 5.44 (d, *J* = 3.4 Hz, 1H, HCOSi), 7.36–7.39 (m, 3H, aromatic H), 7.59–7.62 (m, 2H, aromatic H). – MS (70 eV): *m/z* = 222 [M^+].

$C_{12}H_{18}O_2Si_2$ (222.4) Calcd. C 64.82 H 8.16
Found C 63.97 H 8.20

(Z)-1-(tert-Butyldimethylsilyloxy)-2-ethoxyethene (**15**): Yield starting from **14**, 2.4 g (79%). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.15 (s, 6H, $SiCH_3$), 0.94 [s, 9H, $C(CH_3)_3$], 1.26 (t, *J* = 7.0 Hz, 3H, CH_2CH_3), 3.79 (q, *J* = 7.0 Hz, 2H, $-CH_2-$), 5.34 (d, *J* = 3.4 Hz, HCOEt), 5.48 (d, *J* = 3.4 Hz, 1H, HCOSi).

$C_{10}H_{22}O_2Si$ (202.4) Calcd. C 59.35 H 10.96
Found C 58.51 H 10.76

General Procedure for the Retro-Diels-Alder Reaction Using Gas-Phase Thermolysis[1,2]: Compounds **18**, **20**, **22**, and **24** were thermolyzed in a different manner. Around 35 mmol was slowly evaporated at 120°C/0.01 mbar in a nitrogen stream. The vapor was quickly passed through a quartz tube (250 mm long, 24 mm diameter) filled with quartz chips at 560°C. The product was collected in a trap (−196°C), the anthracene condensing at the outlet of the oven. Products **19**, **21**, **23**, and **25** were analytically pure.

(Z,Z)-2,2,7,7-Tetramethyl-1,3,6,8-tetraoxa-2,7-disilacyclodeca-4,9-diene (**19**): Yield starting from **18**, 7.7 g (95%). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.27 (s, 12H, $SiCH_3$), 5.68 (s, 4H, =CH). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = −2.87 (4 C, $SiCH_3$), 125.9 (4 C, =CH). – MS (70 eV): m/z = 116 [M$^+$, monomeric].

$C_8H_{16}O_4Si_2$ (232.4) Calcd. C 41.35 H 6.94
Found C 40.92 H 7.16
Mol. mass 241 (vapor pressure osmometry)

(Z,Z)-2,2,7,7-Tetraethyl-1,3,6,8-tetraoxa-2,7-disilacyclodeca-4,9-diene (**21**): Yield starting from **20**, 9.0 g (89%). – ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 0.76–0.85 (m, 8H, $SiCH_2$), 0.98–1.08 (m, 12H, $SiCH_2CH_3$), 5.68 (s, 4H, =CH). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 4.00 (4 C, $SiCH_2$), 6.25 (4 C, $SiCH_2CH_3$), 126.01 (4 C, =CH–). – MS (70 eV): m/z = 288 [M$^+$].

$C_{12}H_{24}O_4Si_2$ (288.5) Calcd. C 49.96 H 8.39
Found C 50.31 H 8.44
Mol. mass 309 (in THF, vapor pressure osmometry)

(Z,Z)-2,7-Diethyl-2,7-dimethyl-1,3,6,8-tetraoxa-2,7-disilacyclodeca-4,9-diene (**23**): Yield starting from **22**, 8.4 g (90%) (as a diastereomeric mixture of 1:1). The difference in the ^{1}H-NMR signal for the CH_3 group was $\Delta\delta$ = 0.004. In the following ^{1}H-NMR data this difference will not be considered. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.25 (s, 6H, $SiCH_3$), 0.60–0.80 (m, 4H, $SiCH_2$), 0.97–1.05 (m, 6H, $SiCH_2CH_3$), 5.68 (s, 4H, =CHO). – ^{13}C NMR ($CDCl_3$): Isomer I δ = −5.17 (2 C, $SiCH_3$), 5.68 (2 C, $SiCH_2$), 6.21 (2 C, $SiCH_2CH_3$), 125.96 (4 C, =CH–); Isomer II δ = −5.11 (2 C, $SiCH_3$), 5.77 (2 C, $SiCH_2$), 6.21 (2 C, $SiCH_2CH_3$), 125.96 (4 C, =CH–). – MS (70 eV): m/z = 260 [M$^+$].

$C_{10}H_{20}O_4Si_2$ (260.4)
Mol. mass 267 (in THF, vapor pressure osmometry)

(Z,Z)-2,7-Dimethyl-2,7-diphenyl-1,3,6,8-tetraoxa-2,7-disilacyclodeca-4,9-diene (**25**): Yield starting from **24**, 5.1 g (41%). In contrast to the preparation of **19**, **21**, and **23**, product **25** condensed after thermolysis together with anthracene. Therefore the distillate was dissolved in petroleum ether (40–60°C), anthracene was filtered off and the solvent evaporated. The residue was distilled in a kugelrohr apparatus (100–120°C/0.08 mbar). According to NMR two diastereosisomers were formed with a de of 19%. – ^{1}H NMR ($CDCl_3$, 90 MHz): Main isomer δ = 0.57 (s, 6H, $SiCH_3$), 5.67 (s, 4H, =CHOSi), 7.3–7.5 (m, 6H, aromatic H), 7.57–7.80 (m, 4H, aromatic H); Minor isomer δ = 0.47 (s, 6H, $SiCH_3$), 5.73 (s, 4H, =CHOSi), 7.3–7.5 (m, 6H, aromatic H), 5.57–7.8 (m, 4H, aromatic H). – ^{13}C NMR ($CDCl_3$, 75 MHz): Main isomer δ = −3.23 (2 C, $SiCH_3$), 126.11 (4 C, =CHOSi), 127.93 (4 C, aromatic C-3′, -5′), 130.41 (2 C, aromatic C-4′), 133.23 (2 C, aromatic C-1′), 133.93 (4 C, aromatic C-2′, -6′); Minor isomer δ = −3.84 (2 C, $SiCH_3$), 126.24 (4 C, =CHOSi), 127.87 (4 C, aromatic C-3′, -5′), 130.44 (2 C, aromatic C-4′), 133.16 (2 C, aromatic C-1′), 133.81 (4 C, aromatic C-2′, -6′). – MS (70 eV): m/z = 356 [M$^+$], 341 [M – CH_3], 314 [$C_{16}H_{18}O_3Si_2^+$], 249 [M – Ph], 178 [$C_9H_{10}O_2Si^+$].

$C_{18}H_{20}O_4Si_2$ (356.5) Calcd. C 60,64 H 5.65
Found C 58.97, 59.20 H 5.52, 5.69

Combustion during elemental analysis was always incomplete, and carbon black was formed.

CAS Registry Numbers

1: 2732-95-8 / **3**: 137768-32-2 / **4**: 137768-33-3 / **5**: 26327-98-0 / **6**: 2732-94-7 / **7**: 19191-12-8 / **10**: 137768-34-4 / **11**: 137768-35-5 / **12**: 137768-36-6 / **13**: 137768-37-7 / **14**: 137768-38-8 / **15**: 137768-39-9 / **18**: 137768-40-2 / **19**: 137768-41-3 / **20**: 137768-42-4 / **21**: 137768-43-5 / **22**: 137768-44-6 / **23** (isomer 1): 137768-45-7 / **23** (isomer 2): 137821-46-6 / **24**: 137768-46-8 / **25** (isomer 1): 137768-47-9 / **25** (isomer 2): 137821-47-7

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