The Synthesis of Hetero-bridged [5](3,6)Oxepinophanes

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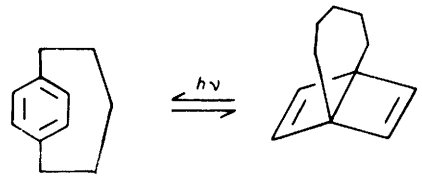
The [5](3,6)oxepinophanes (**8**) are the oxepines with the shortest bridge reported so far. They were obtained starting from diethyl furan-3,4-dicarboxylate (**3**) which, with lithium aluminium hydride, afforded the diol (**4**); this was converted into the seven-membered siloxanes (**5a** and **b**) by reaction with dichlorodimethylsilane or dichlorodimesitylsilane, respectively. By the Prinzbach–Tochtermann sequence, compounds (**5**) were converted into the oxepinophanes (**8**) in three steps: Diels–Alder reaction of (**5**) with dimethyl acetylenedicarboxylate to give the fused 7-oxanobornadienes (**6**), photochemical transformations of compounds (**6**) to the fused 7-oxaquadricyclanes (**7**), and thermal isomerization of compounds (**7**) to (**8**). Attempted conversion of (**8a**) into (**11a**), a derivative of [5]paracyclophane, was unsuccessful.

We have recently obtained [5]paracyclophane (**1**), the smallest representative of the paracyclophane series, by irradiation of its Dewar isomer (**2**) [equation (1)].[1] Not surprisingly, compound (**1**) turned out to be unstable at room temperature; moreover, a photostationary equilibrium between (**1**) and (**2**) was established, which contained only *ca.* 6—7% of (**1**). It was therefore desirable to construct a [5]paracyclophane with higher stability.



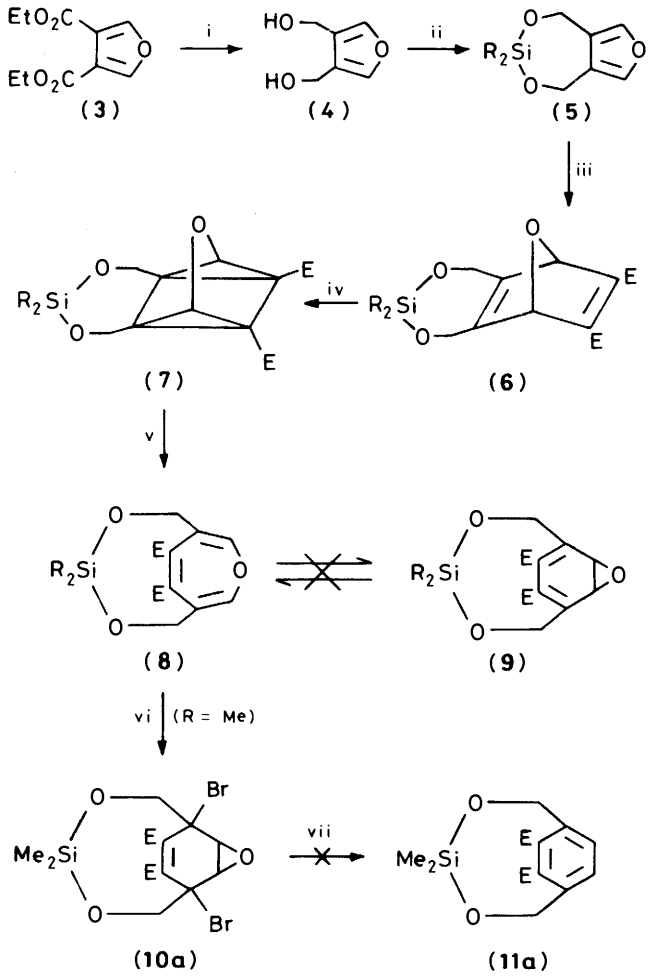
(**1**) (**2**)

The strategy described here is based on the following considerations. Numerous examples illustrate[2–5] that, in small cyclophanes, the strain is distributed between the benzene ring, which responds by bending, and the bridge, which generally exhibits extended bonds and bond angles. One might therefore expect that the strain in the benzene ring could be alleviated by introducing longer and more flexible bonds into the bridge, thereby increasing the overall stability of the molecule. The obvious choice to increase the length and flexibility of the bridge are heteroatoms of higher rows of the Periodic Table.

In previous investigations, we had encountered serious difficulties when attempting the synthesis of hetero-substituted analogues of (**2**) by our traditional route *via* bicyclopropenyls.[6] A different approach to [*n*]paracyclophanes has been developed by Tochtermann *et al.*[4] It makes use of the transformation of furans to oxepines as described by Prinzbach,[7] and has been realized for derivatives of [6]paracyclophane and higher homologues. We felt that the Tochtermann approach might be extended to small [*n*]cyclophanes with heteroatoms in the bridge, as shown for the synthesis of compounds (**8**) in Scheme 1.

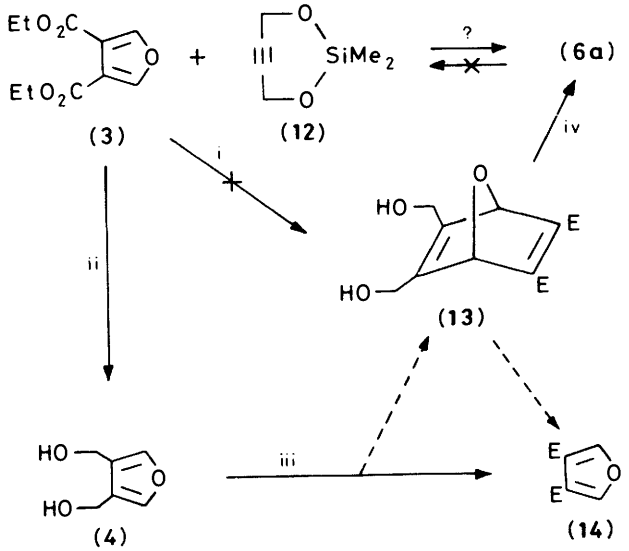
Although we have not yet succeeded in achieving our primary goal of synthesizing a hetero-bridged derivative of [5]paracyclophane, the antepenultimate products of this approach, the hetero-bridged [5](3,6)oxepinophanes (**8**), are of interest in themselves, being the smallest members of oxepines bridged in a '*para*' fashion, *i.e.* with at least two atoms between the bridging positions, known to date.

The preparation of the key intermediate, the oxanorbornadiene (**6**), gave some problems, as illustrated for the dimethyl substituent (**6a**). Originally, we considered or attempted a number of approaches which are summarized in Scheme 2. As they were unpromising or unsuccessful, they will be only briefly commented upon. The most direct synthesis of (**6a**), in line with Tochtermann's original approach,[4a] would be the Diels–Alder



Scheme 1. **a**: R = Me; **b**: R = mesityl; E = CO_2Me; *Reagents and conditions*: i, $LiAlH_4$, Et_2O, reflux; ii, R_2SiCl_2, NEt_3, benzene (high dilution); iii, EC≡CE, benzene, reflux; iv, irradiation (see text); v, *m*-xylene, reflux; vi, Br_2, pyridine; vii, several reducing agents (see text).

reaction of the furan (**3**) with the cyclic acetylene (**12**); the idea was abandoned because compound (**12**) is not known, and is therefore presumably very unstable; moreover, Tochtermann has shown in the meantime that cycloheptyne cannot be made to react with the furan (**3**).[4d] The oxanorbornadiene (**13**) would be an attractive alternative precursor which would furnish our target molecule (**6a**) by reaction with dichlorodimethylsilane and base. This approach was thwarted because compound (**13**) could not be prepared. Diels–Alder reaction of the furan (**3**) with but-2-yne-1,4-diol did not take place, which is not surprising in view of the low Diels–Alder reactivity of both components.[4a] Reduction of compound (**3**) with lithium aluminium hydride gave the diol (**4**) in 65% yield. Its Diels–Alder reactions with dimethyl acetylenedicarboxylate seemed more promising, and in boiling toluene a reaction was observed. Compound (**13**) was, indeed, probably formed but under the reaction conditions it was, at least to a large extent, converted into the furan (**14**) in a retro-Diels–Alder reaction.

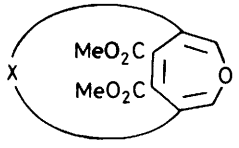


Scheme 2. E = CO_2R; R = Me or Et. *Reagents and conditions*: i, $HOCH_2C{\equiv}CCH_2OH$; ii, $LiAlH_4$; iii, EC≡CE (E = CO_2Me), toluene, reflux; iv, Me_2SiCl_2.

With this experience, we turned to the successful route of Scheme 1. Compound (**4**) was transformed into the furo-siladioxepines (**5**) by reaction with the appropriate dichlorosilane R_2SiCl_2 [**a**; R = Me; **b**; R = mesityl(2,4,6-trimethylphenyl)]. In the case of compound (**5a**), we obtained mostly oligomers or polymers when the reaction was performed under ordinary conditions. However, using high-dilution techniques, the yield of (**5a**) was 61%; under the same conditions, the mesityl analogue (**5b**) was obtained in 12% yield only. Diels–Alder reaction of compounds (**5**) with dimethyl acetylenedicarboxylate gave the desired tricycles (**6**) in 60—70% yield. As we had anticipated, the Diels–Alder reaction did indeed proceed, but in a manner contrary to that for compound (**13**); the retro-Diels–Alder cleavage of (**6**) to (**14**) and (**12**) did not occur because of the high strain in the latter. The two following steps went without particular problems, in accord with the Prinzbach–Tochtermann route. The photochemical isomerization of compounds (**6**) to the oxaquadricyclanes (**7**) was practically quantitative. It was followed by thermal isomerization of compound (**7**) in refluxing *m*-xylene to give the title compounds (**8**).

The yield of compounds (**8**) (*ca.* 25%) was markedly lower than in the unstrained analogues prepared by Prinzbach[7] and Tochtermann.[4d] Obviously, the pentacyclic system (**7**) does not suffer from serious conformational strain, whereas the *anti*-Bredt strain of the cyclophane (**8**), a derivative of *trans*, *trans*-cyclodecadiene, must be considerable. This strain would be even more severe in the arene oxides (**9**), which may be considered to be derivatives of *trans*, *trans*-cyclononadiene. While normal oxepines are usually found to be in equilibrium with their tautomeric arene oxides,[8] we could not detect any of the oxides (**9**) in the cyclophanes (**8**) by ^1H n.m.r. or u.v. spectroscopy. Similar results have been reported by Tochtermann *et al.* in the [6]oxepinophane series.[4b,d]

The [5](3,6)oxepinophanes (**8**) are the representatives of their class with the shortest bridge. In contrast to aromatic systems, the seven-membered rings of the non-aromatic oxepines adopt nonplanar conformations. Consequently, the strain will be considerably reduced compared with that in the benzenoid paracyclophanes. While the ^1H n.m.r. spectra of (**8**) are unexceptional and uninformative in this respect, the u.v. spectra reveal increasing strain in the series (**16**), (**15**), (**8a**) (Table), the long-wavelength absorption shifting from 286 to 276 and 256 nm, respectively. This may be taken as an indication of decreasing conjugation due to increasing nonplanarity in this sequence.



(**8a**) X = $CH_2OSiMe_2OCH_2$
(**15**) X = $[CH_2]_6$
(**16**) X = $[CH_2]_{10}$

Table. U.v. spectra of [*n*](3,6)oxepinophanes[a]

Compound	[*n*]	$\lambda_{max.}$[nm] (log ε)	
(**8a**)[b]	5	226 (3.6)	256 (3.45)
(**15**)[c]	6	203 (4.05)	276 (3.45)
(**16**)[d]	10	213 (4.00)	286 (3.56)

[a] EtOH. [b] This work. [c] Ref. 4*a*. [d] Ref. 4*d*.

It is of interest in this connection that stable [*n*]paracyclophanes in the benzenoid series have so far only been reported for $n \geqslant 6$;[2–5] [5]paracyclophane (**1**) decomposes above 0 °C.[1] However, even for seven-membered aromatic systems such as the [*n*](3,7)tropolonophanes reported by Itô and co-workers, only compounds with $n = 7$ are known while those with $n = 6$ could not be synthesized.[9]

Our attempts to convert compound (**8a**) into the hetero-bridged [5]paracyclophane (**11a**) are so far unsuccessful. According to the method of Tochtermann,[4b] we had hoped to achieve this transformation by addition of bromine to (**8a**), to afford the dibromo epoxide (**10a**), and reduction of the latter with McMurry's reagent[10] to give the target molecule (**11a**). The first step could be achieved in 47% yield, but the second did not yield identifiable products.

Similarly negative results were obtained on attempted

reduction of compound (**10a**) with zinc–copper couple[11] or octacarbonyldicobalt.[12] No volatile, low-molecular products were detected, and ^{1}H n.m.r. spectroscopic analysis indicated that the siloxane bridge had, at least in part, been destroyed. On attempted reduction with diazomalonate–rhodium acetate[13] or sodium iodide–sodium thiosulphate,[14] only starting material (**10a**) was recovered. We therefore prepared compound (**8b**), the dimesityl analogue of (**8a**), because steric hindrance at the vulnerable siloxane moiety may be expected to prevent cleavage reactions. The investigation of compound (**8b**) and similar compounds and of their conversion into analogues of (**11**) is continuing.

Experimental

^{1}H N.m.r. spectra were recorded on a Bruker WH 90 or WM 250 spectrometer at a frequency of 90 MHz or 250 MHz, respectively. All products were analysed by mass spectrometry, using a Varian CH 5 DF mass spectrometer at an ionization potential of 70 eV. U.v. spectra were recorded on a Cary 114 spectrophotometer. All m.p.s were measured on a Buchi, and are uncorrected. Microanalyses were performed by the Instituut voor Toegepaste Chemie TNO, Zeist, The Netherlands, under the supervision of Mr G. J. Rotscheid.

3,4-*Bis*(*hydroxymethyl*)*furan* (**4**).—To a stirred suspension of $LiAlH_4$ (4.5 g, 0.118 mol) in diethyl ether (200 ml) was slowly added a solution of diethyl furan-3,4-dicarboxylate (**3**) (25 g, 0.117 mol) in diethyl ether (80 ml). After the addition, the reaction mixture was heated under reflux for 2.5 h. After the mixture had cooled to room temperature, water (25 ml) and 30% H_2SO_4 (25 ml) were added slowly and the mixture was stirred for 1 h. The organic layer was separated and dried ($MgSO_4$), and the solvent was evaporated off at reduced pressure. The residue was distilled under reduced pressure and gave the *diol* (**4**) as a liquid (9.8 g, 65%), b.p. 95—96 °C at 5 × 10^{-2} mbar*; δ_H (90 MHz; $CDCl_3$) 3.02 (2 H, s, OH), 4.60 (4 H, s, 2 × CH_2), and 7.38 (2 H, s, 2- and 5-H); *m*/*z* 128 (32, $M^{+\cdot}$), 110 (93), 109 (100), and 81 (34) (Found: M^+, 128.0471. $C_6H_8O_3$ requires *M*, 128.0473). Compound (**4**) was previously prepared by the same procedure, but no physical properties have been reported.[14]

4,4*Dimethyl*-3,5,9-*trioxa*-4-*silabicyclo*[5.3.0]*deca*-1(10),7-*diene* (**5a**).—To a stirred solution of triethylamine (15.8 g, 0.156 mol) in benzene (250 ml) were simultaneously added a solution of the diol (**4**) (10 g, 0.078 mol) in benzene (100 ml) and a solution of dichlorodimethylsilane (10 g, 0.078 mol) in benzene (100 ml) during 1 h; a white precipitate of Et_3NHCl formed. After the mixture had been stirred for another 0.5 h, the precipitate was filtered off and the filtrate was evaporated under reduced pressure. The residue was purified by vacuum distillation, to yield crystals of the *title compound* (**5a**), (8.71 g, 61%), m.p. 40 °C; b.p. 60 °C at 5 × 10^{-2} mbar; δ_H (90 MHz; $CDCl_3$) 0.24 (6 H, s, 2 × CH_3), 4.79 (4 H, s, 2 × CH_2), and 7.32 (2 H, s, 8- and 10-H); δ_C (62.89 MHz; $CDCl_3$) −3.4 (q, $^1J_{CH}$ 119 Hz, $SiCH_3$), 56.6 (t, $^1J_{CH}$ 145 Hz, CH_2), 124.9 (s, C-1 and -7), and 139.4 p.p.m. (d, $^1J_{CH}$ 200 Hz, C-8 and -10); *m*/*z* 184 (24, $M^{+\cdot}$), 169 (83), and 139 (100) (Found: M^+, 184.0561. C, 51.3; H, 6.4; Si, 14.9%. $C_8H_{12}O_3Si$ requires *M*, 184.0556. C, 52.15; H, 6.56; Si, 15.24%).

4,4-*Dimesityl*-3,5,9-*trioxa*-4-*silabicyclo*[5.3.0]*deca*-1(10),7-*diene* (**5b**).—The synthesis of compound (**5b**) was performed with diol (**4**) (2.75 g, 21.5 mmol) and dichlorodimesitylsilane (7.23 g, 21.5 mmol) in complete analogy with the preparation of compound (**5a**), and yielded the *title compound* (**5b**) as crystals (1.04 g, 12%), m.p. 111—112 °C; δ_H (90 MHz; $CDCl_3$) 2.25 (6 H, s, 2 × *p*-CH_3), 2.39 (12 H, s, 4 × *o*-CH_3), 4.80 (4 H, s, 2 × CH_2), 6.80 (4 H, s, ArH), and 7.26 (2 H, s, 8- and 10-H); δ_C (62.89 MHz; $CDCl_3$) 21.0 (q, $^1J_{CH}$ 128 Hz, *p*-CH_3), 23.4 (q, $^1J_{CH}$ 127 Hz, *o*-CH_3), 56.6 (t, $^1J_{CH}$ 145 Hz, CH_2), 125.1 (s, C-1 and -7), 128.8 (s, Si–C), 129.2 (d, $^1J_{CH}$ 154 Hz, *m*-C); 138.5 (d, $^1J_{CH}$ 202 Hz, C-8 and -10), 139.7 (s, *p*-C), and 145.2 p.p.m. (s, *o*-C); *m*/*z* 392 (19, $M^{+\cdot}$) and 272 (100) (Found: M^+, 392.1825. C, 72.85; H, 7.2%. $C_{24}H_{28}O_3Si$ requires *M*, 392.1807. C, 74.43; H, 7.19%).

10,11-*Bis*(*methoxycarbonyl*)-5,5-*dimethyl*-4,6,12-*trioxa*-5-*silatricyclo*[7.2.1.0^{2,8}]*dodeca*-2(8),10-*diene* (**6a**).—A mixture of compound (**5a**) (8.35 g, 0.046 mmol) and dimethyl acetylenedicarboxylate (6.53 g, 0.046 mol) in benzene (250 ml) was heated under reflux under nitrogen for 24 h. After the mixture had cooled to room temperature, the solvent was evaporated off at reduced pressure. The residue was purified by recrystallization from n-hexane and gave crystals of the *title compound* (**6a**) (10.41 g, 70%), m.p. 103—104 °C; δ_H (250 MHz; $CDCl_3$) 0.10 (3 H, s, $SiCH_3$), 0.20 (3 H, s, $SiCH_3$), 3.84 (6 H, s, 2 × OCH_3), 4.72 (4 H, AA′BB′ system, δ_A 4.87, δ_B 4.50, J_{AB} 17, $J_{AB'}$ −3, $J_{AA'}$ 3, $J_{BB'}$ 4 Hz, 2 × CH_2), and 5.40 (2 H, s, 1- and 9-H); δ_C (62.89 MHz; $CDCl_3$) −3.4 (q, $^1J_{CH}$ 114 Hz, $SiCH_3$), 52.4 (q, $^1J_{CH}$ 148 Hz, OCH_3), 61.4 (t, $^1J_{CH}$ 147 Hz, CH_2), 87.0 (d, $^1J_{CH}$ 170 Hz, C-1 and -9), 149.3 (s, C-2 and -8), 152.3 (s, C-10 and -11), and 163.0 p.p.m. (s, C=O); *m*/*z* 326 (14, $M^{+\cdot}$) and 169 (100) (Found: M^+, 326.0821. C, 50.6; H, 5.4%. $C_{14}H_{18}O_7Si$ requires *M*, 326.0839. C, 51.52; H, 5.56%).

5,5-*Dimesityl*-10,11-*bis*(*methoxycarbonyl*)-4,6,12-*trioxa*-5-*silatricyclo*[7.2.1.0^{2,8}]*dodeca*-2(8),10-diene (**6b**).—The synthesis of compound (**6b**) was performed analogously to that of (**6a**), starting from compound (**5b**) (0.75 g, 1.9 mmol), and yielded the *title compound* (**6b**) as crystals (0.59 g, 58%), m.p. 80—82 °C; δ_H (250 MHz; $CDCl_3$), 2.22 (3 H, s, *p*-CH_3), 2.25 (3 H, s, *p*-CH_3), 2.27 (6 H, s, 2 × *o*-CH_3), 2.38 (6 H, s, 2 × *o*-CH_3), 3.79 (6 H, s, 2 × OCH_3), 4.73 (4 H, AA′BB′ system, δ_A 4.89, δ_B 4.56, J_{AB} 17, $J_{AA'}$ 3, $J_{BB'}$ 3, $J_{AB'}$ −3 Hz, 2 × CH_2), 5.37 (2 H, s, 1- and 9-H), 6.73 (2 H, s, ArH), and 6.78 (2 H, s, ArH); δ_C (62.89 MHz; $CDCl_3$) 21.0 (q, $^1J_{CH}$ 125 Hz, *p*-CH_3), 23.0 (q, $^1J_{CH}$ 123 Hz, *o*-CH_3), 23.2 (q, $^1J_{CH}$ 123 Hz, *o*-CH_3), 52.3 (q, $^1J_{CH}$ 147 Hz, OCH_3), 60.8 (t, $^1J_{CH}$ 145 Hz, C-3 and -7), 87.1 (d, $^1J_{CH}$ 170 Hz, C-1 and -9), 128.1 (d, $^1J_{CH}$ 152 Hz, *m*-CH), 129.0 (d, $^1J_{CH}$ 152 Hz, *m*-CH), 129.1 (s, Si–C), 139.4 (s, *p*-C), 139.6 (s, *p*-C), 144.5 (s, *o*-C), 144.7 (s, *o*-C), 150.4 (s, C-2 and -8), 152.5 (s, C-10 and -11), and 162.8 p.p.m. (s, C=O); *m*/*z* 534 (7, $M^{+\cdot}$), 399 (74), and 355 (100) (Found: M^+, 534.2079. C, 67.3; H, 7.0%. $C_{30}H_{34}O_7Si$ requires *M*, 534.2070. C, 67.39; H, 6.41%).

2,6-*Bis*(*methoxycarbonyl*)-10,10-*dimethyl*-4,9,11-*trioxa*-10-*silapentacyclo*[5.5.0.0^{1,3}.0^{2,6}.0^{5,7}]*dodecane* (**7a**).—A solution of the tricycle (**6a**) (1.83 g, 5.6 mmol) in diethyl ether (100 ml) was irradiated for 3 h at −20 °C with a mercury lamp (medium pressure; quartz vessel). A filter solution of $NiSO_4 \cdot 6H_2O$ (240 g l^{-1}) and $CoSO_4 \cdot 7H_2O$ (45 g l^{-1}) was employed. After irradiation, the solvent was evaporated off and the residue was purified by recrystallization from n-hexane to give the *title compound* (**7a**) as crystals (1.46 g, 80%), m.p. 112—113 °C; δ_H (90 MHz; $CDCl_3$) 0.22 (3 H, s, $SiCH_3$), 0.24 (3 H, s, $SiCH_3$), 3.75 (6 H, s, 2 × OCH_3), 4.16 (4 H, AB system, δ_A 4.08, δ_B 4.25, J_{AB} 13.6 Hz, 2 × CH_2), and 4.87 (2 H, s, 3- and 5-H); δ_C (62.89 MHz; $CDCl_3$), −5.2 (q, $^1J_{CH}$ 119 Hz, $SiCH_3$), −2.9 (q, $^1J_{CH}$ 120 Hz, $SiCH_3$), 33.5 (s, C-1 and -7), 45.5 (s, C-2 and -6), 52.0 (q, $^1J_{CH}$ 147 Hz, OCH_3), 56.8 (dd, $^1J_{CH}$ 147, $^1J_{CH}$ 144 Hz, C-8 and -12), 74.5 (d, $^1J_{CH}$ 200 Hz, C-3 and -5), and 167.3 p.p.m. (s, C=O); *m*/*z* 326

* 1 mbar = 10^2 Pa.

(1, $M^{+\cdot}$), 311 (2), and 265 (100) (Found: M^+, 326.0830. C, 51.35; H, 5.6%. $C_{14}H_{18}O_7Si$ requires M, 326.0839. C, 51.52; H, 5.56%).

10,10-*Dimesityl*-2,6-*bis*(*methoxycarbonyl*)-4,9,11-*trioxa*-10-*silapentacyclo*[5.5.0.0^{1,3}.0^{2,6}.0^{5,7}]*dodecane* (**7b**).—The synthesis of compound (**7b**) was performed analogously to that of compound (**7a**), starting from the tricycle (**6b**) (0.53 g, 1 mmol), and yielded the *title compound* (**7b**) as crystals (0.32 g, 60%), m.p. 178 °C; δ_H (90 MHz; $CDCl_3$) 2.25 (3 H, s, *p*-CH_3), 2.29 (3 H, s, *p*-CH_3), 2.40 (6 H, s, 2 × *o*-CH_3), 2.45 (6 H, s, 2 × *o*-CH_3), 3.76 (6 H, s, 2 × OCH_3), 4.20 (4 H, AB system, δ_A 4.14, δ_B 4.23, J_{AB} 13 Hz, 2 × CH_2), 4.87 (2 H, s, 3- and 5-H), 6.82 (2 H, s, ArH), and 6.89 (2 H, s, ArH); δ_C (62.89 MHz; $CDCl_3$) 21.1 (q, $^1J_{CH}$ 128 Hz, *p*-CH_3), 23.2 (q, $^1J_{CH}$ 129 Hz, *o*-CH_3), 23.5 (q, $^1J_{CH}$ 129 Hz, *o*-CH_3), 33.9 (s, C-1 and -7), 45.9 (s, C-2 and -6), 51.9 (q, $^1J_{CH}$ 147 Hz, OCH_3), 56.6 (dd, $^1J_{CH}$ 144 Hz, $^1J_{CH}$ 150 Hz, C-8 and -12), 74.5 (d, $^1J_{CH}$ 200 Hz, C-3 and -5), 126.5 (s, Si–C), 129.3 (d, $^1J_{CH}$ 160 Hz, *m*-C), 129.7 (d, $^1J_{CH}$ 160 Hz, *m*-C), 140.0 (s, *p*-C), 140.4 (s, *p*-C), 145.5 (s, *o*-C), 145.8 (s, *o*-C), and 167.4 p.p.m. (s, C=O); *m*/*z* 534 (1, $M^{+\cdot}$), 382 (19), and 149 (100) (Found: M^+, 534.2047. C, 66.7; H, 6.5%. $C_{30}H_{34}O_7Si$ requires M, 534.2070. C, 67.39; H, 6.41%).

11,12-*Bis*(*methoxycarbonyl*)-4,4-*dimethyl*-3,5,9-*trioxa*-4-*silabicyclo*[5.3.2]*dodeca*-1(10),7,11-*triene* (**8a**).—A solution of compound (**7a**) (1.37 g, 4 mmol) in *m*-xylene (300 ml) was heated at 130 °C for 6 h under nitrogen. After the solution had cooled to room temperature, the solvent was evaporated off at reduced pressure. The residue was triturated with n-hexane and gave the *title compound* (**8a**) as crystals (0.33 g, 25%), m.p. 107 °C; $\lambda_{max.}$(EtOH) 256 (log ε 3.45) and 226 nm (3.58); δ_H (90 MHz; $CDCl_3$) 0.02 (3 H, s, $SiCH_3$), 0.13 (3 H, s, $SiCH_3$), 3.85 (6 H, s, 2 × OCH_3), 4.45 (4 H, AB system, δ_A 4.22, δ_B 4.69, J_{AB} 11 Hz, 2 × CH_2), and 6.69 (2 H, s, 8- and 10-H); δ_C (62.89 MHz; $CDCl_3$) −2.8 (q, $^1J_{CH}$ 120 Hz, $SiCH_3$), −0.7 (q, $^1J_{CH}$ 120 Hz, $SiCH_3$), 52.7 (q, $^1J_{CH}$ 148 Hz, OCH_3), 62.7 (t, $^1J_{CH}$ 149 Hz, CH_2), 126.9 (s, C-1 and -7), 136.6 (s, C-11 and -12), 149.6 (d, $^1J_{CH}$ 192 Hz, C-8 and -10), and 165.0 p.p.m. (s, C=O); *m*/*z* 326 (2, $M^{+\cdot}$), 311 (25), and 265 (100) (Found: M^+, 326.0808. C, 51.4; H, 5.6%. $C_{14}H_{18}O_7Si$ requires M, 326.0839. C, 51.52; H, 5.56%).

4,4-*Dimesityl*-11,12-*bis*(*methoxycarbonyl*)-3,5,9-*trioxa*-4-*silabicyclo*[5.3.2]*dodeca*-1(10),7,11-*triene* (**8b**).—The synthesis of compound (**8b**) was performed analogously to that of compound (**8a**), starting from the pentacycle (**7b**) (0.19 g, 0.36 mmol), and yielded the *title compound* (**8b**) as crystals (0.03 g, 16%), m.p. 170—171 °C; δ_H (250 MHz; $CDCl_3$) 2.22 (3 H, s, *p*-CH_3), 2.24 (6 H, s, 2 × *o*-CH_3), 2.26 (3 H, s, *p*-CH_3), 2.30 (6 H, s, 2 × *o*-CH_3), 3.81 (6 H, s, 2 × OCH_3), 4.44 (4 H, AB system, δ_A 4.24, δ_B 4.64, J_{AB} 11 Hz, 2 × CH_2), 6.43 (2 H, s, 8-and 10-H), 6.73 (2 H, s, *m*-CH), and 6.78 (2 H, s, *m*-CH); δ_C (62.89 MHz; $CDCl_3$) 21.0 (q, $^1J_{CH}$ 129 Hz, *p*-CH_3), 23.4 (q, $^1J_{CH}$ 130 Hz, *o*-CH_3), 23.5 (q, $^1J_{CH}$ 130 Hz, *o*-CH_3), 52.4 (q, $^1J_{CH}$ 149 Hz, OCH_3), 61.4 (t, $^1J_{CH}$ 151 Hz, C-2 and -6), 126.6 (s, Si–C), 127.7 (s, C-1 and -7), 129.0 (d, $^1J_{CH}$ 160 Hz, *m*-C), 129.4 (d, $^1J_{CH}$ 160 Hz, *m*-C), 137.4 (s, C-11 and -12), 138.9 (s, *p*-C), 144.2 (s, *o*-C), 144.5 (s, *o*-C), 148.3 (d, $^1J_{CH}$ 198 Hz, C-8 and -10), and 165.2 p.p.m. (s, C=O); *m*/*z* 534 (0.3, $M^{+\cdot}$), 414 (100), and 382 (5) (Found: M^+, 534.2047. $C_{30}H_{34}O_7Si$ requires M, 534.2070).

1,7-*Dibromo*-11,12-*bis*(*methoxycarbonyl*)-4,4-*dimethyl*-3,5,9-*trioxa*-4-*silatricyclo*[5.3.2.0^{8,10}]*dodec*-11-*ene* (**10a**).—To a solution of compound (**8a**) (60 mg, 0.18 mmol) in chloroform (4 ml) was added a solution of bromine (30.4 mg, 0.19 mmol) and pyridine (15 mg, 0.19 mmol) in chloroform (4 ml) and the mixture was stirred for 24 h at room temperature. After addition of water (3 ml), the organic layer was separated, dried ($MgSO_4$), and concentrated at reduced pressure. The residue was triturated with n-hexane and yielded the *title compound* (**10a**) as crystals (42 mg, 47%), m.p. 132 °C; δ_H (90 MHz; $CDCl_3$) 0.14 (3 H, s, $SiCH_3$), 0.18 (3 H, s, $SiCH_3$), 3.83 (6 H, s, 2 × OCH_3), 3.88 (2 H, s, 8- and 10-H), and 4.49 (4 H, AB system, δ_A 4.26, δ_B 4.72, J_{AB} 12 Hz, 2 × CH_2); δ_C (62.89 MHz; $CDCl_3$) −4.4 (q, $^1J_{CH}$ 120 Hz, $SiCH_3$), −3.3 (q, $^1J_{CH}$ 119 Hz, $SiCH_3$), 52.5 (q, $^1J_{CH}$ 148 Hz, OCH_3), 60.4 (s, C-1 and -7), 63.9 (d, $^1J_{CH}$ 189 Hz, C-8 and -10), 68.9 (dd, $^1J_{CH}$ 151, $^1J_{CH}$ 157 Hz, C-2 and -6), 134.5 (s, C-11 and -12), and 164.85 (s, C=O); *m*/*z* 469 (4, $[M - CH_3]^+$), and 377 (100) (Found: $[M - CH_3]^+$, 468.8966. $C_{13}H_{15}Br_2O_7Si$ requires M, 468.8953). Compound (**10a**) was unstable and turned brown even when kept at 0 °C.

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