

55. Preparation and Electrophilic Substitution of 1-Trimethylsilylpentadienyllithium

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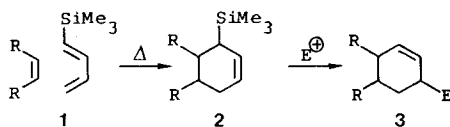
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Summary

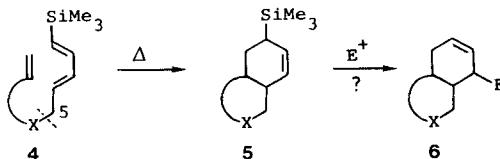
Pentadienyllithium (**16**) was regioselectively and efficiently transformed to 1-trimethylsilyl-2,4-pentadiene (**17**) by reaction with chlorotrimethylsilane (*Scheme 5*). Deprotonation of **17** and subsequent electrophilic attack furnished the regioisomeric products **12** and/or **13** in good yields (*Schemes 5* and *6*). The utility of the reaction **18** → **12** for the convergent assembly of the 1-silyl-1,3-butadiene unit with an olefinic dienophile is further illustrated by the smooth intramolecular *Diels-Alder* reaction **19** → **20**.

Introduction. - Although the synthetic utility of 1-silyl-1,3-butadienes was exemplified by the cycloaddition-substitution sequence **1** → **2** → **3** [1] (*Scheme 1*), these dienes are not easily accessible [1] [2]. We planned to combine the advantages of intramolecular *Diels-Alder* reactions¹⁾ **4** → **5** with the allylic rearrangement and substitution **5** → **6** (*Scheme 2*).

Scheme 1

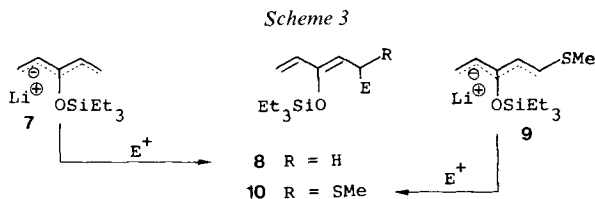


Scheme 2

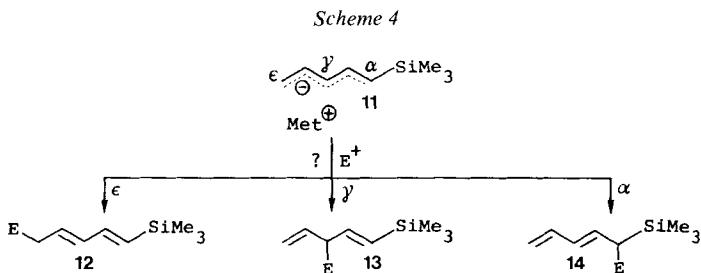


¹⁾ Reviews: [3].

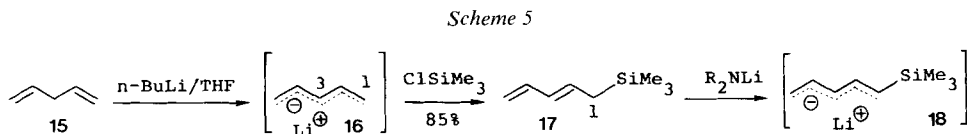
Our first aim was therefore the convergent synthesis of the functionalized trienes **4** by formation of the C(5),X-bond in analogy to the transformations **7**→**8** and **9**→**10** (Scheme 3) [4] [5]²).



This approach initially raised the question of how to prepare the crucial metalated pentadiene **11** (Scheme 4), and particularly as to whether electrophilic attack on **11** would occur at the desired ϵ -site (giving the 1,3-dienes **12**) rather than at the γ - or the α -site (giving **13** or **14**)³.



Preparation and Lithiation of 1-Trimethylsilyl-2,4-pentadiene (Scheme 5). – Penta-dienyllithium (**16**), prepared from 1,4-pentadiene (**15**) [7a]⁴, was smoothly and selectively silylated at C(1) by reaction with chlorotrimethylsilane to furnish the diene **17** in high yield (Scheme 5). The *E*-geometry of **17** (strong IR. band at 1000 cm^{-1} [9]; $^1\text{H-NMR}$. $J(\text{H}-\text{C}(2), \text{H}-\text{C}(3)) = 15\text{ Hz}$), is consistent with the *W*-configuration of pentadienyllithium [7b,c]. The silylation **16**→**17** compares favorably in terms of regio- and stereo-selectivity⁵) with the protonation of **16** [7] [8]⁶). To our knowledge,



²) Recently the silylation **7**→**8**, $\text{E} = \text{SiMe}_3$ was achieved in good yield [5b]. The mass spectrum of **17** but not its preparation has been cited in [13].

³) For electrophilic substitutions of metalated allylsilanes see [6].

⁴) For the preparation of metalated pentadienes from 1,3-pentadiene see [8].

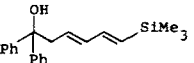
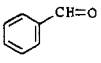
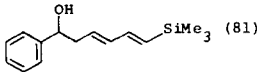
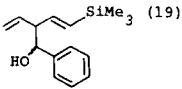
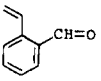
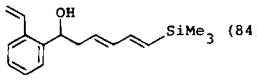
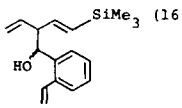
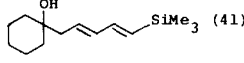
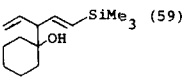
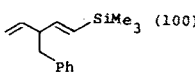
⁵) $^1\text{H-NMR}$. shows the presence of *ca.* 5% of an unidentified isomer.

⁶) For the reaction of metalated methylpentadienes with other electrophiles see [10].

17 is the first 1-silyl-2,4-pentadiene described²); in view of its ready accessibility the diene **17** and its derivatives may be of value in organic synthesis. Deprotonation of **17** with lithium diisopropylamide in tetrahydrofuran (procedure A) or with lithium cyclohexylisopropylamide in dimethoxyethane (procedure B) gave the key intermediate **18**, which was trapped with various electrophiles (*Scheme 6*).

Electrophilic Substitution of 1-Trimethylsilyl-2,4-pentadienyllithium (18) (*Scheme 6*). – The substitution products **12** and/or **13** were generally obtained in good yields but with variable regioselectivity. Thus benzophenone reacted exclusively at the ϵ -position giving the conjugated diene **12a**. Benzaldehyde or *o*-vinylbenzaldehyde also gave preferentially the corresponding 1,3-dienes **12b** and **12c** together with minor amounts of the 1,4-dienes **13b** and **13c**, respectively. With cyclohexanone the regioisomers **12d** and **13d** (1:1.5) were obtained. By contrast, alkylation of **18** with benzyl bromide proceeded with high but reversed selectivity to give solely the product of γ -attack **13e**. In no case could the formation of an α -product **14** be observed. The structures of the products were easily assigned on the basis of their UV., IR., ¹H-NMR. and mass spectra. In contrast to their isomers **13**, the ϵ -products **12** display a strong UV. absorption maximum at 235 to 242 nm ($\log \epsilon = 4.11$ to 4.56), a characteristic IR. band at $\sim 1000\text{ cm}^{-1}$ (out-of-plane-CH-deformation of conjugated (*E*)-alkenes [9]) and in their ¹H-NMR. spectra the vicinal coupling constants $J(\text{H}-\text{C}(1), \text{H}-\text{C}(2)) = 18\text{ Hz}$ and $J(\text{H}-\text{C}(3), \text{H}-\text{C}(4)) = 15\text{ Hz}$ ⁷). The

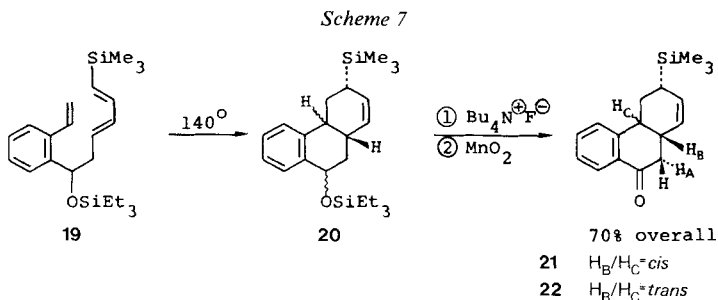
Scheme 6

Entry	Electrophile	ϵ -Product 12 (rel. %)	γ -Product 13 (rel. %)	Yield: 12+13 (Procedure)
a	$\text{Ph}_2\text{C}=\text{O}$	 (100)	—	75% (A)
b		 (81)	 (19)	81% (A) 56% (B)
c		 (84)	 (16)	64% (B)
d		 (41)	 (59)	66% (B)
e	PhCH_2Br	—	 (100)	64% (B)

⁷) Independently derived data on (*E*)-1-trimethylsilyl-1,3-dienes show a UV. maximum (MeOH) at 231 nm ($\log \epsilon = 4.34$) [1d], a characteristic IR. band at 990 to 1005 cm^{-1} [2a,b] and a ¹H-NMR. coupling constant $J(\text{H}-\text{C}(1), \text{H}-\text{C}(2)) = 18\text{ Hz}$ [2b].

γ -products **13** show a IR. band at 911 to 918 cm^{-1} , typical for terminal olefins (also displayed by **12c**) [9] and in their ^1H -NMR. spectra a vicinal coupling constant $J(\text{H}-\text{C}(1), \text{H}-\text{C}(2)) = 18$ Hz. Evidence for a kinetic control of the regiochemistry described here was provided by the non-interconvertibility of the isomers **12d** and **13d** on treatment with lithium cyclohexylisopropylamide in dimethoxyethane at -75° for 3 h. More forcing conditions (potassium hydride/dimethoxyethane/0 to 25°) led only to partial isomerization **13b** $\rightarrow$ **12b** (15% yield) and **13d** $\rightarrow$ **12d** (3% yield). Exchange of the counter ion by treatment of **18** with anhydrous magnesium bromide followed by addition of benzaldehyde afforded an intractable mixture.

Intramolecular Diels-Alder Reaction of the 1-Trimethylsilyl-1,3-butadiene Derivative 19 (Scheme 7). - In order to illustrate the feasibility of the intramolecular *Diels-Alder* reactions **4** $\rightarrow$ **5**, the alcohol **12c** (Scheme 6) was converted to its silyl ether **19** which on heating in refluxing xylene for 3.5 h isomerized smoothly to a mixture of the expected diastereoisomeric hexahydrophenanthrenes **20** (Scheme 7)⁸.



Cleavage of the crude silyl ethers **20** with tetrabutylammonium fluoride followed by oxidation of the resulting alcohols with MnO_2 in benzene gave a 1:1 mixture of the ketones **21** and **22** in 70% overall yield from **19**⁹.

Further work directed towards complete ε -substitution of the 1-silylpentadienyl unit and its use in natural product synthesis is under investigation.

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Experimental Part

General. All reactions were carried out under N_2 . Abbreviations are used for the following reagents and solvents: DME dimethoxyethane, HMPA hexamethylphosphoramide, LDA lithium diisopropylamide, LCIA lithium cyclohexylisopropylamide, and THF tetrahydrofuran. The usual work-up means pouring the cold (-75°) reaction mixture into a well-stirred saturated aqueous solution of NH_4Cl , diluting with water, extracting with CH_2Cl_2 , washing the combined organic layers with saturated aqueous NaCl -solution, drying (Na_2SO_4) and removing the solvent i.v. When LCIA was

⁸) For a related approach to hexahydrophenanthrenes see [10b].

⁹) The less polar ketone was assigned the *cis*-configuration **21** on the basis of the H_B -NMR. signal at $\delta = 2.90$ ppm which shows the vicinal coupling constants $J_{\text{AB}} = 14$ and $J_{\text{BC}} = 4.5$ Hz.

used the resulting ammonium salts could be separated by trituration of the crude reaction mixture with ether. Chromatography was carried out on silica gel (*Merck* 0.05–0.20 mm) unless otherwise specified. Medium-pressure column chromatography was performed on a '*Merck* Lobarfertigsäule Grösse B (310 × 25 mm) Li *Chroprep* Si 60 (40–63 μ m)' coupled with a precolumn of the same type, with toluene or toluene/ethyl acetate 99:1. Gas chromatograms (GC.): column I: glass, 3 mm × 3 m, 5% *Apiezon* L on *Chromosorb* W, 80°, 1 atm N_2 ; column II: glass, 3 mm × 3 m, 3% OV 1 on *Chromosorb* W-HP 80–100 mesh, retention time in min. IR. spectra: CCl_4 , ν_{max} in cm^{-1} . UV. spectra: hexane unless otherwise specified, λ_{max} in nm, log ϵ in parentheses. 1H -NMR. spectra: in $CDCl_3$ at 100 MHz unless otherwise specified, internal standard tetramethylsilane ($\delta = 0$ ppm); abbreviations: *s* singlet, *d* doublet, *t* triplet, *qa* quadruplet, *m* multiplet, *br.* broad, *J* spin-spin coupling constant (Hz). MS.: signals are given in *m/z* (rel.%).

1-Trimethylsilyl-2,4-pentadiene (17) (Scheme 5). 1.5*N* Butyllithium in hexane (13.4 ml, 20.0 mmol) was added to a mixture of 3.6*N* 1,4-pentadiene **15** in hexane (5.6 ml, 20.0 mmol) and dry THF (40 ml) at -60° . The solution was allowed to warm to 0° over 30 min and then stirred for 1 h at 5 to 10° . The resulting orange-red mixture was cooled to -70° , and chlorotrimethylsilane (2.6 ml, 20.5 mmol) was added to the stirred orange-red mixture at -70° . After complete addition the mixture became colorless and a precipitate started to separate. The mixture was stirred at -70° for 5 min, then subjected to the usual work-up (using pentane for extraction). The organic layers were evaporated at 0° . The oily residue after chromatography (hexane) and bulb-to-bulb distillation at 105° (bath/760 Torr) furnished 1-trimethylsilyl-2,4-pentadiene (**17**) as a colorless oil (2.47 g, 88%), used without further purification for the following experiments. For analysis the diene **17** was purified by chromatography on silica gel, impregnated with 5% $AgNO_3$ (hexane/benzene 4:1) and distilled. GC.: (column I) retention time 8.4. – IR. ($CHCl_3$): 3080, 3010, 1800_w, 1640, 1597, 1255, 1145, 1005, 950, 895, 850. – UV.: 234 (4.31). – 1H -NMR.: 0.04 (*s*, 9 H); 1.56 (*d*, *J* = 7, 2 H); 4.90 (*d* × *d*, *J* = 2 and 10, 1 H); 5.04 (*d* × *d*, *J* = 2 and 17, 1 H); 5.77 (*d* × *t*, *J* = 15 and 7, 1 H; irradiation at 1.56 → *d*, *J* = 15); 5.93 (*d* × *d*, *J* = 9 and 15, 1 H); 6.36 (*d* × *t*, *J* = 9, 10 and 17, 1 H). – MS.: 140 ($C_8H_{16}Si^+$, 11), 125 (3), 109 (1), 97 (2), 75 (4), 74 (8), 73 (100), 59 (10), 45 (10).

1-(Trimethylsilyl)pentadienyllithium (18). – *Procedure A.* To a stirred solution of freshly distilled diisopropylamine (0.11 g, 1.1 mmol) in dry THF (2 ml) was added dropwise at -20° 1.50*N* butyllithium in hexane (0.70 ml, 1.05 mmol). The mixture was allowed to warm to 5° and, after addition of HMPA (0.20 ml, 1.15 mmol) was stirred at 5° for 10 min. A solution of 1-trimethylsilyl-2,4-pentadiene (**17**) (0.143 g, 1.0 mmol) in THF (1 ml) was then added at -30° . The mixture was allowed to warm to 0° over 30 min, then was stirred at 5 – 10° for 30 min and finally allowed to react with various electrophiles at -75° .

Procedure B. To a solution of freshly distilled *N*-cyclohexylisopropylamine (0.466 g, 3.3 mmol) in dry DME (6 ml) was added dropwise at -20° 1.42*N* butyllithium in hexane (2.22 ml, 3.15 mmol) followed by HMPA (0.58 ml, 3.15 mmol). After stirring for 20 min at -20° the mixture was cooled to -70° and a solution of freshly distilled 1-trimethylsilyl-2,4-pentadiene (**17**) (0.42 g, 3.0 mmol) in DME (3 ml) was added dropwise. The mixture was allowed to warm to 0° over 1 h, then stirred at 5° for 1.5 h and finally allowed to react with various electrophiles at -75° .

Electrophilic Substitution of 1-(Trimethylsilyl)pentadienyllithium (Scheme 6): – (E,E)-1,1-Diphenyl-6-trimethylsilyl-3,5-hexadien-1-ol (**12a**). A solution of benzophenone (0.20 g, 1.1 mmol) in THF (1 ml) was added slowly at -75° to a stirred solution of 1-(trimethylsilyl)pentadienyllithium (**18**) (1.0 mmol) in THF, prepared *in situ* (procedure A, LDA). Usual work-up, followed by chromatography (toluene/hexane/ether 60:38:2) gave, together with unchanged benzophenone (0.041 g), only the conjugated diene **12a** (oil). – UV. (MeOH): 204 (4.44), 242 (4.56). – IR. ($CHCl_3$): 3590, 3550, 3020_w, 1640, 1600, 1580, 1496, 1450, 1350, 1255, 1005, 865, 840. – 1H -NMR.: 0.06 (*s*, 9 H); 2.53 (*s*, 1 H; disappears on treatment with D_2O); 3.14 (*d*, *J* = 7, 2 H); 5.59 (*d* × *t*, *J* = 14 and 7, 1 H; irradiation at 3.14 → *d*, *J* = 14); 5.84 (*d*, *J* = 18, 1 H); 6.15–6.62 (2 H); 7.2–7.6 (10 H). – MS.: (M^+ not observed), 307 ($C_{21}H_{26}OSi^+ - OH$, 2), 255 (6), 184 (17), 183 (100), 140 (2), 125 (2), 109 (1), 106 (2), 105 (23), 77 (8), 73 (4).

(E,E)-1-Phenyl-6-trimethylsilyl-3,5-hexadien-1-ol (**12b**) and (E)-1-Phenyl-4-trimethylsilyl-2-vinyl-3-buten-1-ols (**13b**). *Procedure B.* A solution of freshly purified benzaldehyde [11] (0.191 g, 1.8 mmol) in dry DME (1 ml) was added dropwise to 0.33*N* 1-(trimethylsilyl)pentadienyllithium (**18**) (freshly prepared, procedure B, LCIA) in DME (6 ml, 2 mmol) at -75° . The mixture was stirred at -75°

for 30 min to give after the usual work-up and filtration through silica gel (hexane/ether 3:1) an oily residue which was subjected to medium pressure chromatography (toluene/ethyl acetate 99:1) to give as the least polar product one diastereoisomer of **13b** (oil, 0.035 g, 8% yield). - UV.: 210 (3.90), 287 (3.30). - IR.: 3620, 3570, 1615, 1500, 1460, 1252s, 1215, 1000, 911s, 870s, 846s, 700s. - ¹H-NMR.: 0.08 (s, 9 H); 2.20 (d, J=3, 1H); 3.13 (qa, J=7, 1H); 4.64 (d×d, J=7 and 3, 1H; irradiation at 3.13→br. s); 5.00 (m, 1H; irradiation at 3.13→d×d, J=2 and 10); 5.1 (m, 1H); 5.70 (m, 1H; irradiation at 3.13→br. d, J=17); 5.80 (d, J=18, 1H); 6.07 (d×d, J=7 and 18, 1H; irradiation at 3.13→d, J=18); 7.33 (s, 5 H). - MS.: (M⁺ not observed), 213 (1), 179 (11), 140 (31), 125 (22), 107 (89), 73 (100).

This substance was followed by the more polar diastereoisomer of **13b** (oil, 18 mg, 4%). - UV.: 212 (3.99), 234 (3.79). - IR.: 3620, 3580, 1615, 1500, 1460, 1252s, 1000, 920, 915, 870s, 845s, 700s. - ¹H-NMR.: -0.04 (s, 9 H); 2.18 (d, J=3, 1H); 3.07 (qa, J=7, 1H); 4.60 (d×d, J=3 and 7, 1H; irradiation at 3.07→br. s); 5.13 (d×d, J=2 and 11, 1H); 5.27 (d×d, J=2 and 5, 1H); 5.57 (d, J=18, 1H); 5.65-6.10 (2 H); 7.30 (s, 5 H). - MS.: (M⁺ not observed), 213 (1), 179 (12), 140 (33), 125 (24), 107 (97), 79 (34), 73 (100).

Further elution afforded mixed fractions (59 mg) and finally the major product **12b** (oil, 0.139 g, 44% yield). - UV.: 235 (4.22). - IR.: 3620, 1645w, 1585, 1500, 1460, 1250s, 1005s, 870s, 845s, 703s. - ¹H-NMR.: 0.08 (s, 9 H); 2.06 (d, J=2, 1H); 2.57 (t, J=7, 2 H); 4.76 (br. t, J=7, 1H; irradiation at 2.57→br. s); 5.72 (d×t, J=15 and 7, 1H; irradiation at 2.57→d, J=15); 5.81 (d, J=18, 1H); 6.22 (d×d, J=10 and 15, 1H); 6.54 (d×d, J=10 and 18); 7.38 (s, 5 H). - MS.: (M⁺ not observed), 231 (4), 179 (12), 140 (37), 125 (23), 107 (100), 79 (37), 73 (70).

Procedure A. A solution of purified benzaldehyde [11] (0.071 g, 0.67 mmol) in THF (1 ml) was added dropwise to a stirred 0.67N solution of 1-trimethylsilyl-2,4-pentadienyllithium (**18**) (procedure A) in THF (1.5 ml, 1.0 mmol) at -70°. After stirring at -70° for 30 min and the usual work-up, repeated chromatography (hexane/ether 4:1) gave a 1:2 mixture of unchanged benzaldehyde and the 2 diastereoisomers of **13b** (0.043 g) and the more polar conjugated diene **12b** (0.109 g, 66% yield).

(E,E)-6-Trimethylsilyl-1-(2-vinyl-1-phenyl)-3,5-hexadien-1-ol (**12c**) and (E)-4-Trimethylsilyl-2-vinyl-1-(2-vinyl-1-phenyl)-3-buten-1-ols (**13c**). A solution of freshly distilled o-vinylbenzaldehyde [12] (0.357 g, 2.7 mmol) in DME (2 ml) was added dropwise to stirred 0.5N 1-trimethylsilyl-2,3-pentadienyllithium **17** in DME (6 ml, 3.0 mmol) (procedure B) at -75°. The mixture was stirred at -75° for 30 min and worked up as usual. Repeated medium-pressure chromatography (toluene/ethyl acetate 99:1) gave the γ-products **13c** as a mixture of diastereoisomers (0.079 g, 10% yield) from which the less polar isomer (oil) could be isolated. - UV.: 205 (4.32), 239 (3.20), 282 (3.48). - IR.: 3620w, 1250, 1000, 920, 870, 845. - ¹H-NMR.: 0.05 (s, 9 H); 2.00 (br. s, 1H); 3.20 (qa, J=7, 1H); 5.05 (d, J=7, 1H; irradiation at 3.20→s); 6.11 (d×d, J=7 and 18, 1H; irradiation at 3.20→d, J=18); 4.80-6.00 (6 H); 6.80-7.70 (5 H). - MS.: 270 (C₁₇H₂₄OSi⁺-2, 5), 205 (20), 140 (36), 133 (100).

Further elution afforded the more polar conjugated diene **12c** (oil, 0.40 g, 54% yield). - UV.: 208 (4.19), 236 (4.19). - IR.: 3610, 1585w, 1485w, 1250s, 1000s, 920, 870s, 845s. - ¹H-NMR.: 0.05 (m, 9 H); 2.00 (s, 1H); 2.55 (m, 2 H); 5.08 (t, J=6.5, 1H; irradiation at 2.55→s); 5.35 (d×d, J=2 and 11, 1H); 6.64 (d×d, J=2 and 17, 1H); 5.77 (d×d×d, J=6, 7 and 15, 1H; irradiation at 2.55→d, J=15); 5.82 (d, J=18, 1H); 6.23 (d×d, J=9 and 15, 1H); 6.55 (d×d, J=9 and 18, 1H); 7.06 (d×d, J=11 and 17, 1H); 7.2-7.4 (4 H). - MS.: 272 (C₁₇H₂₄OSi⁺, 2.5), 205 (23), 182 (19), 180 (15), 167 (12), 141 (16), 140 (14), 133 (100).

(E,E)-1-(5-Trimethylsilyl-2,4-pentadienyl)cyclohexanol (**12d**) and (E)-1-(5-Trimethylsilyl-1,4-pentadien-3-yl)cyclohexanol (**13d**). A solution of freshly distilled cyclohexanone (0.177 g, 1.8 mmol) in dry DME (2 ml) was added dropwise to stirred 0.4N 1-(trimethylsilyl)pentadienyllithium (**18**) (procedure B), in DME (5 ml, 2 mmol) at -75°. After stirring at -75° for 30 min and the usual work-up, chromatography (hexane/ether 9:1) of the reaction mixture gave the less polar γ-product **13d** (oil). - UV.: 213 (3.08). - IR.: 3560, 1635w, 1605, 1445, 1245s, 995, 960, 910, 860s, 830s. - ¹H-NMR.: 0.07 (s, 9 H); 1.3-1.8 (11H); 2.75 (t, J=8, 1H); 5.06 (m, 1H; irradiation at 2.75→d×d, J=2 and 10.5); 5.19 (d×d, J=2 and 6, 1H); 5.74 (d, J=18, 1H); 5.95 (m, 1H); 6.14 (d×d, J=8 and 18, 1H; irradiation at 2.75→d, J=18). - MS.: (M⁺ not observed), 171 (38), 140 (53), 109 (5), 99 (82), 81 (36), 75 (18), 73 (100).

After mixed fractions (0.047 g), further elution afforded the conjugated diene **12d** (oil). - UV.: 235 (4.11). - IR.: 3580, 1640w, 1570w, 1450, 1245s, 1000s, 860s, 830s. - ¹H-NMR.: 0.08 (s, 9 H); 1.3-1.7 (11H); 2.25 (d, J=7.5, 2 H); 5.77 (d, J=18, 1H); 5.80 (d×t, J=15 and 7.6, 1H; irradiation at

2.25 $\rightarrow d$, $J=15$); 6.18 ($d \times d$, $J=9$ and 15, 1H); 6.56 ($d \times d$, $J=9$ and 18, 1H). – MS.: (M^+ not observed), 223 (7), 171 (23), 140 (34), 125 (30), 99 (100), 81 (59), 73 (80), 59 (23), 55 (16).

(E)-3-Benzyl-1-trimethylsilyl-4-pentadiene (**13e**). A solution of freshly distilled benzyl bromide (0.308 g, 1.8 mmol) in DME (1 ml) was added dropwise to 0.5N 1-(trimethylsilyl)pentadienyllithium (**18**) (procedure B) in DME (4 ml, 2 mmol) at -75° . After stirring at -75° for 30 min and the usual work-up, chromatography (hexane/ether 98:2) of the reaction mixture gave only the γ -product **13b** (oil, 0.265 g, 64% yield). – UV.: 215 (3.35), 256 (2.34). – IR.: 1640w, 1612, 1500, 1458, 1252s, 994s, 918s, 870s, 845s. – $^1\text{H-NMR}$.: 0.12 (s, 9H); 2.84 (m, 2H); 3.14 (quintuplett, $J=7$, 1H); 5.01 (m, 1H; irradiation at 3.14 $\rightarrow d \times d$, $J=2$ and 7); 5.14 (m, 1H); 5.67 (d, $J=18$, 1H); 5.89 ($d \times d \times d$, $J=7$, 10 and 16, 1H; irradiation at 3.14 $\rightarrow d \times d$, $J=10$ and 16); 6.10 ($d \times d$, $J=7$ and 18, 1H; irradiation at 3.14 $\rightarrow d$, $J=18$); 7.1–7.5 (5H). – MS.: 230 ($\text{C}_{15}\text{H}_{22}\text{Si}^+$, 10), 215 (10), 156 (14), 91 (90), 73 (100), 59 (28).

Intramolecular Diels-Alder Reaction of the 1-Trimethylsilyl-1,3-butadiene Derivative 19 (Scheme 7). – (E,E)-1-Triethylsilyloxy-6-trimethylsilyl-1-(2-vinyl-1-phenyl)-3,5-hexadiene (**19**). Triethylsilylchloride (0.27 ml, 1.62 mmol) was added dropwise to a mixture of the alcohol **12c** (0.400 g, 1.47 mmol) and imidazole (0.123 g, 1.78 mmol) in dry dimethylformamide (5 ml) at 0° . The reaction mixture was stirred at 0° for 1.5 h, then diluted with pentane and poured into ice-water. Extraction with pentane, washing of the extracts with sat. aq. NaCl-solution, drying (Na_2SO_4), evaporation of the solvent and rapid chromatography of the residue through Al_2O_3 (activity III, hexane) furnished the silyl ether **19** (oil, 0.520 g, 92% yield). – UV.: 207 (4.39), 238 (4.60). – IR.: 1645w, 1580w, 1250s, 1075s, 1005, 870s, 845s. – $^1\text{H-NMR}$.: 0.06 (s, 9H); 0.3–1.0 (15H); 2.43 (t, $J=6$, 2H); 4.98 (t, $J=6$, 1H); 5.30 ($d \times d$, $J=2$ and 11, 1H); 5.59 ($d \times d$, $J=2$ and 17, 1H); 5.70 (m, 1H); 5.72 (d, $J=18$, 1H); 6.0 ($d \times d$, $J=9$ and 15, 1H); 6.47 ($d \times d$, $J=9$ and 18, 1H); 7.06 ($d \times d$, $J=11$ and 17, 1H); 7.1–7.6 (4H). – MS.: (M^+ not observed), 248 (16), 247 (100), 217 (5), 189 (3), 115 (4).

3-Trimethylsilyl-3,4,4a,9,10,10a-hexahydrophenanthren-9-ones **21** and **22**. A solution of the triene **19** (0.487 g, 1.26 mmol) in oxygen-free xylene was heated under reflux for 3.5 h. Evaporation of the solvent and chromatography of the residue (hexane/ CH_2Cl_2 4:1) furnished the crude cycloadduct **20** (mixture of diastereoisomers) which was stirred with tetrabutylammonium fluoride (0.3 g, 0.94 mmol) in THF (5 ml) at 25° for 10 min. Evaporation of the solvent and rapid chromatography of the residue (hexane/ether 2:1) furnished a mixture of diastereoisomeric alcohols (0.328 g). This was stirred with activated MnO_2 (1.4 g) in dry benzene (8 ml) at 25° for 4 h. Filtration of the reaction mixture through *Celite*, followed by evaporation gave the ketones **21** and **22** as an oily residue (1.5:1 by NMR. evidence; GC. (column II, 200°): 1 peak, retention time 11.5) which was partially separated by chromatography (toluene) to give apart from the mixture **21** + **22** (0.140 g) the less polar ketone (oil, 0.052 g). – UV.: 207 (4.18), 239 (3.94), 284 (3.13), 292 (3.11). – IR.: 1692s, 1600, 1460, 1300s, 1290s, 1253s, 1100, 900, 855s, 842s. – $^1\text{H-NMR}$. (400 MHz): 0.01 (s, 9H); 1.70 (m, 1H); 1.8–1.9 (2H); 2.41 ($d \times d$, $J=14$ and 17.5, 1H); 2.70 ($d \times d$, $J=4.5$ and 17.5, 1H); 2.90 ($d \times t$, $J=14$ and 4.5, 1H); 3.00 (m, 1H); 5.76 (m, 2H); 7.3–7.5 (3H); 8.00 (m, 1H). – MS.: 270 ($\text{C}_{17}\text{H}_{22}\text{OSi}^+$, 58), 255 (16), 242 (11), 229 (13), 216 (13), 203 (11), 180 (13), 179 (14), 165 (21), 73 (100), 59 (84).

This was followed by the more polar ketone (oil, 0.017 g). – UV.: 207 (4.22), 241 (4.04), 284 (3.20), 292 (3.18). – IR.: 1695s, 1600, 1455, 1292s, 1253s, 1153, 910, 850s, 842s. – $^1\text{H-NMR}$. (400 MHz): 0.00 (s, 9H); 1.7–1.8 (2H); 2.22 ($d \times d$, $J=14$ and 17, 1H); 2.50 (m, 2H); 2.60 (m, 1H); 2.74 ($d \times d$, $J=3.5$ and 17, 1H); 5.35 ($d \times t$, $J=2$ and 9, 1H); 5.72 (m, 1H); 7.2–7.5 (3H); 7.98 ($d \times d$, $J=2$ and 7, 1H). – MS.: 270 ($\text{C}_{17}\text{H}_{22}\text{OSi}^+$, 34), 255 (16), 216 (5), 180 (14), 179 (14), 171 (10), 165 (22), 140 (12), 125 (11), 99 (31), 73 (100).

Isomerization Experiments. – Treatment of 1-(5-Trimethylsilyl-1,4-pentadien-3-yl)cyclohexanol **13d** and 1-(5-Trimethylsilyl-2,4-pentadienyl)cyclohexanol (**12d**) with LCIA in DME. A solution of **13d** (0.040 g, 0.17 mmol) in dry DME (0.5 ml) was added dropwise to stirred 0.3N LCIA in DME (freshly prepared, 0.5 ml, 0.17 mmol) at -75° . The mixture was stirred at -75° for 3 h to give after usual work-up a colorless oil (0.039 g, 98% yield) identified as unchanged **13d** by TLC. (hexane/ether 4:1) and $^1\text{H-NMR}$. evidence. Under identical conditions the conjugated diene **12d** also remained unchanged.

Partial Isomerization of 4-Trimethylsilyl-2-vinyl-1-(2-vinyl-1-phenyl)-3-buten-1-ols (13c**) to 6-Trimethylsilyl-1-(2-vinyl-1-phenyl)-3,5-hexadien-1-ol (**12c**).** Potassium hydride (0.006 g) was added at 0° to a stirred solution of **13c** (0.067 g, 0.25 mmol) in dry THF (2 ml). The mixture was stirred at 0° for 1 h (no conversion observed) and then at 25° for 15 min. Usual work-up and chromatography (toluene)

of the reaction mixture furnished a complex mixture of non-polar hydrocarbons and the conjugated diene **12c** (0.010 g, 15% yield), identified by TLC. and ¹H-NMR.

Partial Isomerization of 1-(5-Trimethylsilyl-1,4-pentadien-3-yl)cyclohexanol 13d to 1-(5-Trimethylsilyl-2,4-pentadienyl)cyclohexanol (12d). A solution of **13d** (0.045 g, 0.19 mmol) in dry THF (0.5 ml) was added to a stirred suspension of potassium hydride (0.009 g, 0.22 mmol) in THF (0.5 ml) containing HMPA (40:1). The mixture was stirred at 0° for 80 min; monitoring of the reaction by TLC. showed the slow disappearance of **13d** and the formation of at least 4 more polar products. Usual work-up and chromatography (hexane/ether 9:1) of the reaction mixture gave recovered **13d** (0.004 g, 9% yield) and the desired conjugated diene **12d** (1.5 mg, 4% yield). Initial addition of 18-crown-6 to the reaction mixture did not affect the reaction.

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