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55. Preparation and Electrophilic Substitution of 1-Trimethylsilylpentadienyllithium

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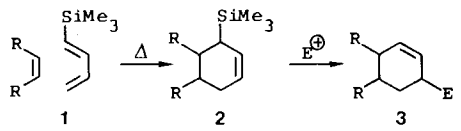
Summary

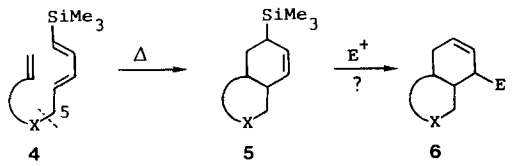
Pentadienyllithium (**16**) was regioselectively and efficiently transformed to 1-trimethylsilyl-2,4-pentadiene (**17**) by reaction with chlorotrimethylsilane *(Scheme 5)*. Deprotonation of **17** and subsequent electrophilic attack furnished the regioisomeric products **12** and/or **13** in good yields (*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* reactions[1]) **4** → **5** with the allylic rearrangement and substitution **5** → **6** *(Scheme 2)*.

Scheme 1



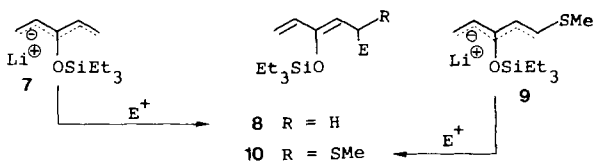
Scheme 2



[1]) Reviews: [3].

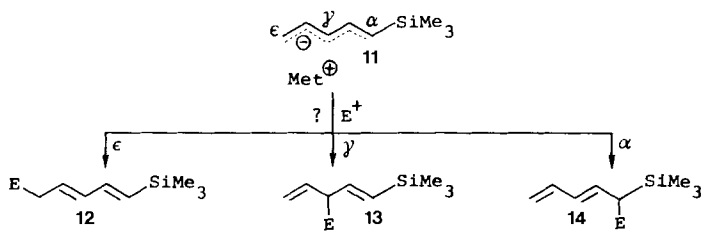
Our first aim was therefore the convergent synthesis of the functionalized trienes **4** by formation of the C(5),X-bond in analogy to the transformations **7**→**8** and **9**→**10** *(Scheme 3)* [4] [5][2]).

Scheme 3



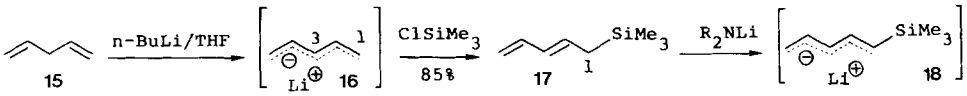
This approach initially raised the question of how to prepare the crucial metalated pentadiene **11** *(Scheme 4)*, and particularly as to whether electrophilic attack on **11** would occur at the desired ε-site (giving the 1,3-dienes **12**) rather than at the γ- or the α-site (giving **13** or **14**)[3]).

Scheme 4



Preparation and Lithiation of 1-Trimethylsilyl-2,4-pentadiene *(Scheme 5)*. – Pentadienyllithium (**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}H-NMR. J(H–C(2),H–C(3))= 15 Hz), is consistent with the *W*-configuration of pentadienyllithium [7b,c]. The silylation **16**→**17** compares favorably in terms of regio- and stereo-selectivity[5]) with the protonation of **16** [7] [8][6]). To our knowledge,

Scheme 5



[2]) Recently the silylation **7**→**8**, E= $SiMe_3$ 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].

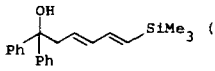
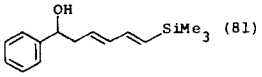
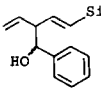
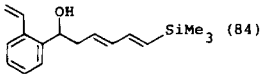
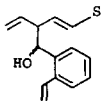
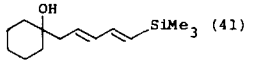
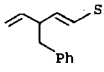
[5]) ^{1}H-NMR. shows the presence of *ca.* 5% of an unidentified isomer.

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

17 is the first 1-silyl-2,4-pentadiene described[2]); 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., ^{1}H-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 ($\log\varepsilon = 4.11$ to 4.56), a characteristic IR. band at $\sim$1000 cm^{-1} (out-of-plane-CH-deformation of conjugated (*E*)-alkenes [9]) and in their ^{1}H-NMR. spectra the vicinal coupling constants $J(\text{H}-\text{C}(1),\text{H}-\text{C}(2)) = 18$ Hz and $J(\text{H}-\text{C}(3),\text{H}-\text{C}(4) = 15$ Hz[7]). The

Scheme 6

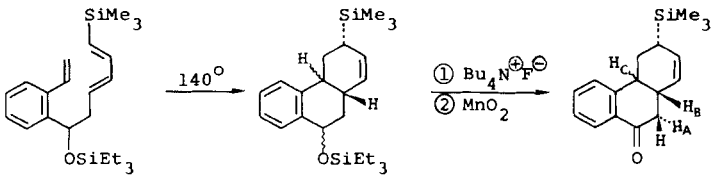
Entry	Electrophile	ε-Product **12** (rel.%)	γ-Product **13** (rel.%)	Yield: **12**+**13** (Procedure)
a	$Ph_2C{=}O$	 (100)	———	75% (A)
b		 (81)	 (19)	81% (A) 56% (B)
c		 (84)	 (16)	64% (B)
d		 (41)	 (59)	66% (B)
e	$PhCH_2Br$	———	 (100)	64% (B)

[7]) Independently derived data on (*E*)-1-trimethylsilyl-1,3-dienes show a UV. maximum (MeOH) at 231 nm ($\log\varepsilon = 4.34$) [1d], a characteristic IR. band at 990 to 1005 cm^{-1} [2a,b] and a ^{1}H-NMR. coupling constant $J(\text{H}-\text{C}(1),\text{H}-\text{C}(2)) = 18$ 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 ^{1}H-NMR. spectra a vicinal coupling constant $J(H-C(1),H-C(2))=18$ 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**→**12b** (15% yield) and **13d**→**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**→**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].

Scheme 7



19 **20**

70% overall

21 H_B/H_C = *cis*

22 H_B/H_C = *trans*

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.

Financial support of this work by the *Swiss National Science Foundation, Sandoz Ltd.*, Basel, and *Givaudan SA*, Vernier, is gratefully acknowledged. We thank Mr. *J. P. Saulnier* for NMR. measurements and Mrs. *F. Klöti* for carrying out the mass spectra.

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 $J_{AB}=14$ and $J_{BC}=4.5$ 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 μm)' 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 I 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. ^{1}H-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 give in *m/z* (rel.%).

1-Trimethylsilyl-2,4-pentadiene (**17**) (Scheme 5). 1.5N Butyllithium in hexane (13.4 ml, 20.0 mmol) was added to a mixture of 3.6N 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). – ^{1}H-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° 1.50N 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° 1.42N 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. – ^{1}H-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 0.33N 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, 1252*s*, 1215, 1000, 911*s*, 870*s*, 846*s*, 700*s*. – ^{1}H-NMR.: 0.08 (*s*, 9 H); 2.20 (*d*, *J*=3, 1 H); 3.13 (*qa*, *J*=7, 1 H); 4.64 (*d*×*d*, *J*=7 and 3, 1 H; irradiation at 3.13→br. *s*); 5.00 (*m*, 1 H; irradiation at 3.13→*d*×*d*, *J*=2 and 10); 5.1 (*m*, 1 H); 5.70 (*m*, 1 H; irradiation at 3.13→br. *d*, *J*=17); 5.80 (*d*, *J*=18, 1 H); 6.07 (*d*×*d*, *J*=7 and 18, 1 H; 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, 1252*s*, 1000, 920, 915, 870*s*, 845*s*, 700*s*. – ^{1}H-NMR.: −0.04 (*s*, 9 H); 2.18 (*d*, *J*=3, 1 H); 3.07 (*qa*, *J*=7, 1 H); 4.60 (*d*×*d*, *J*=3 and 7, 1 H; irradiation at 3.07→br. *s*); 5.13 (*d*×*d*, *J*=2 and 11, 1 H); 5.27 (*d*×*d*, *J*=2 and 5, 1 H); 5.57 (*d*, *J*=18, 1 H); 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, 1645*w*, 1585, 1500, 1460, 1250*s*, 1005*s*, 870*s*, 845*s*, 703*s*. – ^{1}H-NMR.: 0.08 (*s*, 9 H); 2.06 (*d*, *J*=2, 1 H); 2.57 (*t*, *J*=7, 2 H); 4.76 (br. *t*, *J*=7, 1 H; irradiation at 2.57→br. *s*); 5.72 (*d*×*t*, *J*=15 and 7, 1 H; irradiation at 2.57→*d*, *J*=15); 5.81 (*d*, *J*=18, 1 H); 6.22 (*d*×*d*, *J*=10 and 15, 1 H); 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), 2.39 (3.20), 282 (3.48). – IR.: 3620*w*, 1250, 1000, 920, 870, 845. – ^{1}H-NMR.: 0.05 (*s*, 9 H); 2.00 (br. *s*, 1 H); 3.20 (*qa*, *J*=7, 1 H); 5.05 (*d*, *J*=7, 1 H; irradiation at 3.20→*s*); 6.11 (*d*×*d*, *J*=7 and 18, 1 H; irradiation at 3.20→*d*, *J*=18); 4.80–6.00 (6 H); 6.80–7.70 (5 H). – MS.: 270 ($C_{17}H_{24}OSi^+$−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, 1585*w*, 1485*w*, 1250*s*, 1000*s*, 920, 870*s*, 845*s*. – ^{1}H-NMR.: 0.05 (*m*, 9 H); 2.00 (*s*, 1 H); 2.55 (*m*, 2 H); 5.08 (*t*, *J*=6.5, 1 H; irradiation at 2.55→*s*); 5.35 (*d*×*d*, *J*=2 and 11, 1 H); 6.64 (*d*×*d*, *J*=2 and 17, 1 H); 5.77 (*d*×*d*×*d*, *J*=6, 7 and 15, 1 H; irradiation at 2.55→*d*, *J*=15); 5.82 (*d*, *J*=18, 1 H); 6.23 (*d*×*d*, *J*=9 and 15, 1 H); 6.55 (*d*×*d*, *J*=9 and 18, 1 H); 7.06 (*d*×*d*, *J*=11 and 17, 1 H); 7.2–7.4 (4 H). – MS.: 272 ($C_{17}H_{24}OSi^+$, 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, 1635*w*, 1605, 1445, 1245*s*, 995, 960, 910, 860*s*, 830*s*. – ^{1}H-NMR.: 0.07 (*s*, 9 H); 1.3–1.8 (11 H); 2.75 (*t*, *J*=8, 1 H); 5.06 (*m*, 1 H; irradiation at 2.75→*d*×*d*, *J*=2 and 10.5); 5.19 (*d*×*d*, *J*=2 and 6, 1 H); 5.74 (*d*, *J*=18, 1 H); 5.95 (*m*, 1 H); 6.14 (*d*×*d*, *J*=8 and 18, 1 H; 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, 1640*w*, 1570*w*, 1450, 1245*s*, 1000*s*, 860*s*, 830*s*. – ^{1}H-NMR.: 0.08 (*s*, 9 H); 1.3–1.7 (11 H); 2.25 (*d*, *J*=7.5, 2 H); 5.77 (*d*, *J*=18, 1 H); 5.80 (*d*×*t*, *J*=15 and 7.6, 1 H; irradiation at

2.25→*d*, *J*=15); 6.18 (*d*×*d*, *J*=9 and 15, 1H); 6.56 (*d*×*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-1,4-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.: 1640*w*, 1612, 1500, 1458, 1252*s*, 994*s*, 918*s*, 870*s*, 845*s*. – ^{1}H-NMR.: 0.12 (*s*, 9H); 2.84 (*m*, 2H); 3.14 (*quintuplett*, *J*=7, 1H); 5.01 (*m*, 1H; irradiation at 3.14→*d*×*d*, *J*=2 and 7); 5.14 (*m*, 1H); 5.67 (*d*, *J*=18, 1H); 5.89 (*d*×*d*×*d*, *J*=7, 10 and 16, 1H; irradiation at 3.14→*d*×*d*, *J*=10 and 16); 6.10 (*d*×*d*, *J*=7 and 18, 1H; irradiation at 3.14→*d*, *J*=18); 7.1–7.5 (5H). – MS.: 230 ($C_{15}H_{22}Si^+$, 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.: 1645*w*, 1580*w*, 1250*s*, 1075*s*, 1005, 870*s*, 845*s*. – ^{1}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*×*d*, *J*=2 and 11, 1H); 5.59 (*d*×*d*, *J*=2 and 17, 1H); 5.70 (*m*, 1H); 5.72 (*d*, *J*=18, 1H); 6.0 (*d*×*d*, *J*=9 and 15, 1H); 6.47 (*d*×*d*, *J*=9 and 18, 1H); 7.06 (*d*×*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.: 1692*s*, 1600, 1460, 1300*s*, 1290*s*, 1253*s*, 1100, 900, 855*s*, 842*s*. – ^{1}H-NMR. (400 MHz): 0.01 (*s*, 9H); 1.70 (*m*, 1H); 1.8–1.9 (2H); 2.41 (*d*×*d*, *J*=14 and 17.5, 1H); 2.70 (*d*×*d*, *J*=4.5 and 17.5, 1H); 2.90 (*d*×*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 ($C_{17}H_{22}OSi^+$, 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.: 1695*s*, 1600, 1455, 1292*s*, 1253*s*, 1153, 910, 850*s*, 842*s*. – ^{1}H-NMR. (400 MHz): 0.00 (*s*, 9H); 1.7–1.8 (2H); 2.22 (*d*×*d*, *J*=14 and 17, 1H); 2.50 (*m*, 2H); 2.60 (*m*, 1H); 2.74 (*d*×*d*, *J*=3.5 and 17, 1H); 5.35 (*d*×*t*, *J*=2 and 9, 1H); 5.72 (*m*, 1H); 7.2–7.5 (3H); 7.98 (*d*×*d*, *J*=2 and 7, 1H). – MS.: 270 ($C_{17}H_{22}OSi^+$, 34), 255 (16), 215 (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}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 ^{1}H-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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