Organometallics **1992**, *11*, 1565–1575

Carbanions. 26. Formation of Hexadienyl Anions by the Reactions of Various Hexadienes with Cesium Solutions in the Presence of 18-Crown-6 or with *n*-Butyllithium–Cesium *tert*-Butoxide

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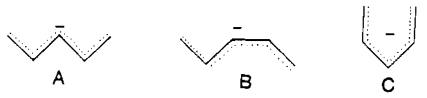
The formation of hexadienyl anions has been studied with cesium as counterion. 1,4-, 2,4-, or 1,5-Hexadiene can be deprotonated with Cs·18-crown-6 solutions and/or with *n*-BuLi·CsO-*t*-Bu in THF to provide hexadienyl anions, and their geometry was revealed by chemical derivatization using trimethylsilylation or carbonation reactions. *trans*-1,4-Hexadiene (1) at –75 °C gave a mixture of exo-W-shaped anion as the major and exo-S-shaped anion as the minor product. *cis*-1,4-Hexadiene (10) under similar conditions produced endo-W-shaped anion as the major and endo-S-shaped anion as the minor product. *cis,trans*-2,4-Hexadiene (11) with *n*-BuLi·CsO-*t*-Bu at –75 °C likely gave a mixture of endo-W-shaped and exo-S-shaped anions, while *trans,trans*-2,4-hexadiene (12) gave the exo-W-shaped anion. At room temperature, in short duration reactions of 1 and 12, exo-S and/or endo-U anion was the major product. Storage of these anions derived from any diene at room temperature for long durations produced an equilibrated mixture of anions which on silylation gave hexadienyltrimethylsilanes 3 and 4 as major products. The equilibration of these anions was faster in presence of catalytic amount of *n*-Bu$_2$Hg or at higher temperature (e.g., 65 °C). Biallyl (13) is metalated by the Cs·18-crown-6 solution at –75 °C and formed a mixture of endo-15, as major product, exo-14, as minor product, which isomerized to 15 in 10 h and finally isomerized to give the equilibrated conjugated hexadienyl anions as the major product.

Introduction

The chemistry of pentadienyl metals has been a recent subject of considerable interest.[1,2] Pentadienyl anions can exist in three planar configurations, zigzag-like W (A),



sickle-like S (B), or horseshoe-like U-shaped (C) ions. Extended Huckel calculations by Hoffman and Olofson[3] and CNDO/2 by Bushby et al.[4] predict that the U-shaped anion should be preferred over the W- or S-shaped anions. However, MNDO calculations[5] predict that the W-shaped structure is more stable than the U- and S-shaped structures by about 3.7 and 1.0 kcal/mol, respectively, for the pentadienyl anion. (Pentadienyl-,[6] (hexadienyl-,[7] and (2-methylpentadienyl)lithium in THF and pentadienyl-,[8] and hexadienylpotassium[9] in liquid ammonia are reported to exist preferentially as W-shaped anions. Schlosser et al.[10] has reported evidence for U-shaped structures for (2-methyl-, and (2,4-dimethylpentadienyl)potassium in THF based on chemical derivatization of anions. Predominance of the U-shaped structure for pentadienylpotassium has also be claimed by Yasuda et al.[11] They have also demonstrated the formation of an exo-U- or exo-S-shaped anion or a mixture of these two for the hexadienyl anions.[11]

Pentadienyl anions can be generated by the metalation of 1,3- and 1,4-dienes in THF with *n*-BuLi,[6] *sec*-BuLi, *n*-BuLi·KO-*t*-Bu, or ((trimethylsilyl)methyl)potassium.[10] While 1,4-dienes can similarly be metalated with potassium in liquid ammonia,[8,9] 1,3-dienes commonly undergo polymerization with alkali metals[12] although Yasuda et al.[11] were successful in the preparation of pentadienyl anions starting from any diene in the presence of a tertiary amine. Cesium metal in THF in the presence of 18-crown-6 forms a dark blue solution which provides a strong reducing medium. The reactive species in such solutions may be an electride, Cs$^+$·18-crown-6·e$^-$, or a ceside, Cs$^+$·18-crown-6·Cs$^-$.[13] The product[14] of the reaction of *n*-BuLi and KO-*t*-Bu ("LICKOR"[14d] reagent) is reported to be a strong base and has been utilized for the metalation of alkenes. The analogous RLi·CsO-*t*-Bu reagent can also be used to prepare organocesium-like compounds.[15] A prior definitive paper has appeared on the metalation of (*Z*)- and (*E*)-1,4-decadiene by *sec*-BuLi with and without KO-*t*-Bu.[14e]

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Table I. Silylation Products from Reactions of *trans*-1,4-Hexadiene (1) with Cs Solutions or with *n*-BuCs in THF

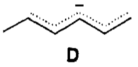
				relative mol %				
run	metalation reagent[a]	temp,[b] °C	time	2[c]	3[c]	4	5	others[d]
1	A	−75	5 min	69	22	4[f]	1[f]	4
2	A	−75	1 h	68	23	5[f]	1[f]	3
3	B	−75	6 h	61	28	6[f]	1[f]	4
4	C	−75	1 h	60	30	5[f]	1[f]	4
5	D	−75	1 h	61	29	3[f]	1[f]	6
6	C	22	1 h	19	72	4[f]	2[f]	3
7	C	22	24 h	11	68	9	5	7
8	C	21	3 d	6	49	24	14	7
		21	6 d	9	50	20	14	7
9	C	g		8	84	0	0	8
10	C	65	45 min	22	36	25	12	5
11	D	22	1 h	32	32	27	8	1
12[e]	C	21	24 h	8	46	24	14	8
		21	4 d	3	50	26	14	7

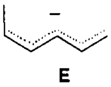
[a] Metalation reagents: A, Cs·18-crown-6 (1:1); B, Cs·18-Crown-6 (2:1); C, *n*-BuCs; D, *n*-BuCs·18-crown-6 (1:1). [b] All reactions were carried out at −75 °C before raising to the final value and time specified. [c] 2 and 3 are not separable under GC conditions used; values for them were obtained by dividing GC % in the ratio obtained from $-CH_2SiMe_3$ integrations in ^1H NMR. [d] Includes branched chain isomers. [e] In presence of catalytic amount (1–2%) of n-Bu_2Hg. [f] Arise from some 5% *cis*-1,4-hexadiene in 1. [g] 21 °C for 1 h and then −75 °C for 2 h.

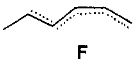
In this paper we report (1) the use of Cs·18-crown-6 solutions for the metalation of 1,4- or 1,5-hexadienes, (2) the use of *n*-BuLi·CsO-*t*-Bu for the metalation of 1,4- or 2,4-hexadienes, (3) the configurations of hexadienyl anions at different temperatures on the basis of chemical derivatization, and (4) the catalytic effect of n-Bu_2Hg in isomerization of these anions. Chemical derivatization of organoalkali metal compounds (such as reaction with carbon dioxide or trimethylsilyl chloride) is a reasonable method for determination of geometrical configuration of hexadienylalkali metal compounds because their rate of reaction with such reagents (rate of reaction ≃ rate of mixing) exceeds their rate of isomerization (cf. Tables I and IV–VII in this work). Chemical derivatization is reported to be often superior to spectroscopic methods for determination of the complex composition of configurational isomers of (2-methylpentadienyl)potassium,[10] (2,4-dimethylpentadienyl)potassium,[10] and related organometallic compounds.[14d–f]

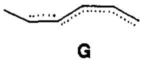
Results and Discussion

Cesium metal can be dissolved in THF in the presence of 1 equiv of 18-crown-6 to give a deep blue solution. The reactive species in such solutions may be an electride, $Cs^+{\cdot}18\text{-crown-}6{\cdot}e^-$. Using a 2:1 ratio of Cs and 18-crown-6, 1.7 mol of Cs can be dissolved per mole of crown ether. Such solutions may now have ceside, $Cs^+{\cdot}18\text{-crown-}6{\cdot}Cs^-$, as the reactive species. *n*-Butylcesium[16] was prepared in situ by the reaction of CsO-*t*-Bu and *n*-BuLi in THF at −75 °C. CsH was generated by a procedure similar to that of Schleyer et al.[17] The following eight configurations are possible for fully conjugated hexadienyl anions:


D
exo-W

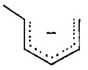

E
endo-W

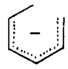

F
exo-S


G
endo-S

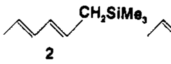

H
exo-S′


I
endo-S′


J
exo-U


K
endo-U

Formation of anions I and K is less likely due to steric reasons.[11b] Silylation of the hexadienyl anions provided mainly straight chain isomers (>90% by GC analysis) and minor quantities of branched chain isomer as reported earlier.[1,11] Silylation of D and H will give hexadienyltrimethylsilane (2), F and J will give 3, E and I will give 4, and G and K will give 5.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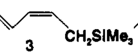
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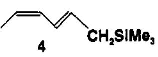
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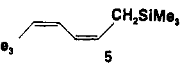
5

Reactions of *trans*-1,4-Hexadiene (1). The diene 1 reacts readily with cesium solutions in THF and 18-crown-6 at −78 °C:

$$1 + Cs{\cdot}18\text{-crown-}6 \rightarrow (CH_3CH\underset{\cdots}{-}CH\underset{\cdots}{-}CH\underset{\cdots}{-}CH\underset{\cdots}{-}CH_2)^-{\cdot}Cs^+ + \tfrac{1}{2}H_2 \quad (1)$$

The yield of the product was 60% (based on active Cs) in 5 min (as judged by carbonation or silylation) and 86% in 1 h. The deep blue color of Cs·18-crown-6 solution was changed to yellow-orange in 5 min, indicating that all cesium in electride or ceside form has been consumed. This observation suggests a two-step mechanism for this reaction (eqs 2 and 3). The formation of hydrogen and CsH just after disappearance of the deep blue color in the reaction mixture was confirmed by measurement of the volume of gas evolved both before and after addition of methanol (see Experimental Section). Also we have shown in an independent experiment that CsH (prepared by an independent route, *n*-BuCs + H_2) in the presence of 18-crown-6 can metalate 1 in 22% yield in 1 h. The relatively low yield of metalated product from preformed CsH may be due to the lower rate of solution or a decreased rate of reaction because of a larger particle size for preformed CsH. This preformed CsH reacts slowly with biallyl under similar conditions (4% yield of metalated product in 1 h) and faster with allylbenzene (65% yield in 15 min).

$$RH + 2Cs^+{\cdot}18\text{-crown-}6{\cdot}e^- \rightarrow R^-Cs^+{\cdot}18\text{-crown-}6 + Cs^+{\cdot}18\text{-crown-}6{\cdot}H^- \quad (2)$$

$$RH + Cs^+{\cdot}18\text{-crown-}6{\cdot}H^- \rightarrow R^-Cs^+{\cdot}18\text{-crown-}6 + H_2 \quad (3)$$

The analyses and identification of carbonation and silylation products by ^1H NMR spectroscopy (Table II), GC, and MS show that the hexadienyl anions formed in the above reaction consisted of a mixture of D and F in about a 3:1 ratio (Scheme I). The two straight chain isomers 2 and 3 from the silylation experiment are not separable under our GC conditions (see Experimental Section); however, chemical shifts and coupling constants for them

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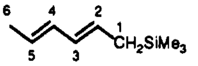
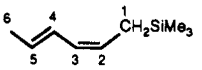
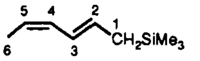
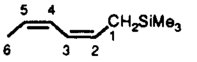
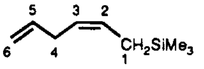
[16] For simplicity the metalating agent produced by the combination of *n*-BuLi and CsO-*t*-Bu will be referred to as *n*-BuCs even though the *n*-BuCs from the metathesis is likely coaggregated to LiO-*t*-Bu.

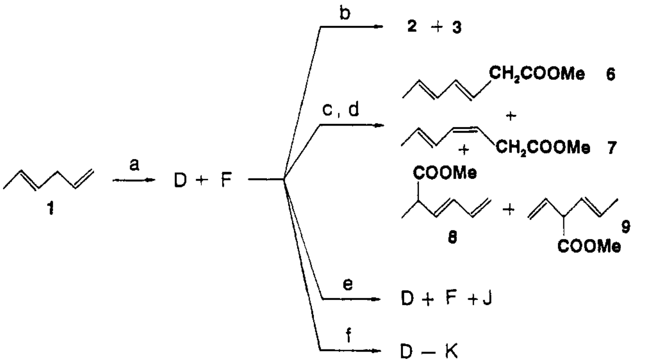
[17] Klusener, P. A. A.; Brandsma, L.; Verkruijsse, H. D.; Schleyer, P. v. R.; Friedel, T.; Pi, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 465–466.

Table II. ^{1}H NMR Chemical Shifts (δ Values) and Coupling Constants (Hz, in Parentheses) for Hexadienyltrimethylsilanes in $CDCl_3$ at Ambient Temperature

product	no.	C_1-*H*	C_2-*H*	C_3-*H*	C_4-*H*	C_5-*H*	C_6-*H*	-Si*Me*$_3$
	2^a	1.47 (d, 8.2)	5.53 (d t, 14.6, 8.2)	5.86 (d d, 14.6, 10.2)	6.00 (d d q, 14.4, 10.2, 1.7)	5.46 (d q, 14.4, 6.4)	1.70 (d, 6.4)	0.11 (s)
	3^a	1.61 (d, 8.9)	5.32 (d t, 10.6, 8.9)	5.87 (pseudo t, 10.6)	6.25 (d d q, 14.7, 10.9, 1.2)	5.60 (d q, 14.7, 5.9)	1.75 (d, 5.9)	0.005 (s)
	4^b	1.54 (d, 8.5)	5.64 (d q, 14.9, 8.4)	6.16 (d d q, 15.0, 11.1, 1.2)	5.94 (pseudo t q, 10.9, 1.6)	5.25 (d q, 10.8, 7.0)	1.70 (d d, 6.9, 1.5)	-0.002 (s)
	5^b	1.62 (d, 8.5)	5.51 (d t d, 10.7, 8.6, 1.7)	overlapping with 4, 6.23-6.14	overlapping with 4, 6.23-6.14	5.42 (d q d, 10.4, 7.2, 1.6)	1.72 (d d, 7.2, 1.3)	-0.002 (s)
	21^b	1.47 (d d, 8.6, 1.4)	5.42 (d t t, 10.7, 8.6, 1.6)	5.27 (d d t, 10.7, 8.6, 1.6)	2.74 (pseudo t, 6.7)	5.79 (d d t, 17.1, 10.1, 6.3)	5.02 (trans, d d, 17.1, 2.0), 4.95 (cis, d d, 10.2, 2.0)	-0.01 (s)

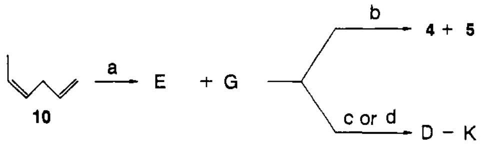
^{a}300 MHz. ^{b}400 MHz.

Scheme I^a



^{a}Key: (a) Cs·18-crown-6 (1:1) or *n*-BuCs (with or without 18-crown-6), THF, -75 °C; (b) Me_3SiCl; (c) CO_2; (d) CH_2N_2; (e) 21 °C for 1 h; (f) 21 °C for 3-7 days or *n*-Bu_2Hg (1-2%).

Scheme II^a



^{a}Key: (a) Cs·18-crown-6 (1:1) or *n*-BuCs, THF, -75 °C; (b) Me_3SiCl; (c) 22 °C for 1 h; (d) 22 °C for 1-3 days or *n*-Bu_2Hg (1-2%).

were calculated from 300-MHz ^{1}H NMR spectra. Pure **2** was isolated by the reaction of *trans,trans*-2,4-hexadiene with *n*-BuCs (details follow) and used as a standard for identification. The data for **3** are consistent with a previous report.[11b] Carbonation of the hexadienyl anions provided more complex mixtures of acids resulting from the attack of CO_2 on C_1, C_3, and C_5 atoms. The formation of **8** ruled out the formation of the anions H and J as the bond between C_3 and C_4 is trans and support the structure of D and F.

Reactions of **1** with Cs or *n*-BuCs solutions with or without 18-crown-6 have been studied under variable conditions, and data are summarized in Table I. Products **4** and **5** in low-temperature runs are due to 5% impurity of *cis*-1,4-hexadiene (**10**) in the starting material **1** (see Scheme II). A perusal of the data reveals that the ratio of carbanions D and F from Cs and 18-crown-6 is independent of time at -75 °C (runs 1-3). *n*-Butylcesium (with or without 18-crown-6) reacts with **1** to give similar products (runs 4 and 5). The stereochemistry of these hexadienyl anions seems to be temperature dependent. When the reaction mixture was allowed to warm to room temperature for 1 h in the absence of 18-crown-6, carbanion F and/or J was the major product (run 6), which slowly equilibrated to a mixture of carbanions D-K on extending the reaction time to 3-6 days (runs 7 and 8). Carbanion D at lower temperature is the major kinetic product which was partially equilibrated at room temperature in 1 h to give F/J as major products. Compound F (J) did not isomerize back to D on reducing the temperature to -75 °C (run 9). At still higher temperature (65 °C) this equilibration was much more rapid (run 10). The presence of 18-crown-6 (run 11) or 2% *n*-Bu_2Hg[18] (run 12) catalyzed the equilibration of the system.

Reactions of **1** with Cs·18-crown-6 solution at -75 °C were also followed by carbonation and esterification of the resulting acids with diazomethane and produced a mixture of four esters **6-9** (GC area % analysis: **6** and **7**, 76; **8**, 9; **9**, 15). This mixture was separated into two fractions by column chromatography on silica gel using 0.5% diethyl ether solution in hexane as eluting solvent. The first fraction contains **6** and **7** (these two esters are not separable by GC under the conditions we used; however, chemical shifts and coupling constants for both isomers were calculated from 400-MHz ^{1}H NMR). The other fraction contains esters **8** and **9**. Compound **8** was identified by independent synthesis via reaction of the dilithium salt of sorbic acid with methyl iodide in a manner similar to that of Fujita et al.,[19] the GC retention time and MS of the methyl ester of this product were identical to that of the compound from the cesium product. ^{1}H NMR data for **9**[20] were obtained by substracting the spectrum of **8** from the spectrum of the mixture of **8** and **9**. These data are summarized in Table III. The carbon skeletons of esters **6-9** were also established by hydrogenation of the mixture of these esters, which gave a mixture of methyl *n*-heptanoate from **6** and **7**, methyl 2-methylhexanoate from **8**, and methyl 2-ethylpentanoate from **9** in the same GC area percent as **6-9** in the original mixture. The identity of the saturated esters was confirmed by comparison with the GC/MS of authentic samples.

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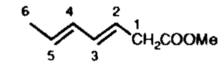
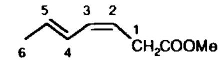
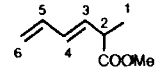
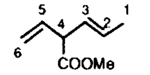
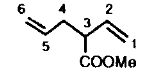
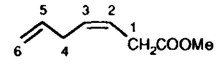
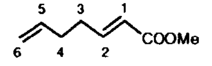
(18) Moret, E.; Furrer, J.; Schlosser, M. *Tetrahedron* **1988**, *44*, 3539-3550.

(19) Fujita, T.; Watanabe, S.; Suga, K.; Nagase, T. *Isr. J. Chem.* **1974**, *12*, 971-976.

(20) A reaction of sorbyl chloride with Mg followed by carbonation gave $CH_3CH{=}CHCH(COOMe)CH{=}CH_2$.[21] GC/MS and hydrogenation of the reaction mixture showed that it is a mixture of cis and trans isomers of this ester. GC of a mixture of this product with the carbonation product from the reactions of 1 and 10 further confirms the identity of 9 and unknown 1.

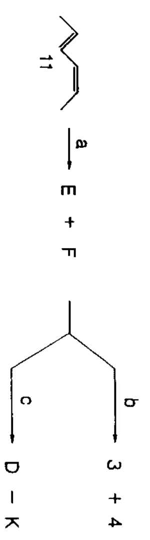
(21) Reichstein, von T.; Trivelli, G. *Helv. Chim. Acta* **1933**, *16*, 968-975.

Table III. ^1H NMR (400 MHz) Chemical Shifts (δ Values) and Coupling Constants[a] (Hz, in Parentheses) for Methyl Esters of Heptadienoic Acids in $CDCl_3$ at Ambient Temperature

product	no.	C_1-*H*	C_2-*H*	C_3-*H*	C_4-*H*	C_5-*H*	C_6-*H*	COO*Me*
	6	3.09 (d d, 7.4, 1.4)	5.61 (d t, 14.7, 7.4)	6.09 (d d t, 14.5, 10.4, 1.4)	6.04 (d d q, 15.0, 10.4, 1.6)	5.65 (d q, 15.0, 7.1)	1.74 (d d, 7.1, 1.6)	3.68 (s)
	7	3.20 (d d, 7.5, 1.4)	5.44 (d pseudo q, 10.6, 7.5, 0.8)	not resolved[c]	6.25 (d d q d, 15.2, 11.0, 1.6, 1.0)	5.77 (d q, 15.2, 7.4)	1.79 (d d, 7.4, 1.6)	3.69 (s)
	8	1.29 (d, 7.0)	3.19 (pseudo quintet, 7.0)	5.76 (d d, 15.1, 10.4)	6.13 (d d, 15.1, 10.4)	6.31 (d t, 17.1, 10.4)	5.18 (trans, d d, 17.1, 1.6), 5.07 (cis d d, 10.0, 1.6)	3.69 (s)
	9[b]	1.71 (d d, 5.0, 0.7)	5.59 (d q, 15.3, 5.0)	5.55 (d d, 15.3, 6.2)	under O*Me*	5.93 (d d d, 17.0, 10.6, 7.5)	5.14 (trans d, 17.5), 5.15 (cis, d, 9.7)	3.70 (s)
	16	5.15 (trans, d t, 17.3, 1.0), 5.15 (cis, d t, 10.2, 1.0)	5.83 (d d d, 17.3, 10.2, 8.2)	3.12 (d t, 7.5, 8.2)	2.51 (d t t, 14.2, 7.1, 1.2), 2.32 (d t t, 14.2, 7.0, 1.3)	5.74 (d d t, 17.1, 10.2, 7.1)	5.07 (trans, d q, 17.1, 1.6), 5.04 (cis, d q, 10.2, 1.0)	3.69 (s)
	17	3.11 (d, 6.1)	5.66 (d t, 10.5, 6.1)	5.61 (d t, 10.5, 7.1)	2.81 (pseudo t, 6.1)	5.80 (d d t, 17.1, 10.1, 6.2)	5.05 (trans, d q, 17.1, 1.8), 5.00 (cis, d q, 10.1, 1.6)	3.69 (s)
	18[b]	5.84 (d, 15.6)	6.97 (d t, 15.6, 6.6)	2.30 (q, 6.6)	2.23 (q, 6.5)	5.78 (complex m)	5.04 (trans, d, 15.7), 5.00 (cis d, 10.0)	3.72 (s)

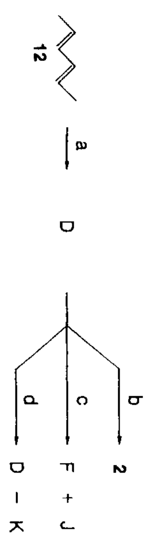
[a] Sometimes coupling constants were calculated from decoupled spectra. [b] 300 MHz. [c] Interference from other signals.

Scheme III[a]



[a] Key: (a) *n*-BuCs with or without 18-crown-6, –75 °C, THF; (b) Me_3SiCl; (c) 21 °C, 1 h to 5 days.

Scheme IV[a]



[a] Key: (a) *n*-BuCs with or without 18-crown-6, THF, –75 °C; (b) Me_3SiCl; (c) 21 °C, 2 h; (d) 21 °C, 1–4 days.

Reactions of *cis*-1,4-Hexadiene (10). Diene **10** reacts with Cs•18-crown-6 or *n*-BuCs solutions at –75 °C to give hexadienyl carbanions E and G (2:1 ratio) in 78% yield in 1 h (Scheme II) as evidenced by silylation and carbonation of the resulting reaction mixture. Reactions of **10** with Cs•18-crown-6 or *n*-BuCs solutions under various conditions are summarized in Table IV. A perusal of data reveals that the ratio of the products remains unchanged on increasing reaction time up to 6 days (runs 1 and 2). When the reaction mixture was allowed to warm to room temperature, it began to equilibrate to a mixture of carbanions D–K (runs 3–5) as in the case of hydrocarbon **1**. This equilibration was again catalyzed and brought to completion by 2% Bu_2Hg (Table IV, runs 6 and 7; Table I, run 12). Carbonation of the reaction mixture obtained by the reaction of **10** with Cs•18-crown-6 at –75 °C gave **8** as the product of CO_2 attack on C_5, which within the accuracy of the data rules out the formation of anions I and K and supports the formation of E and G.

Reactions of *cis,trans*-2,4-Hexadiene (11). Attempted reactions of **11** (and also **12**) with a solution of Cs•18-crown-6 in THF at –75 °C gave a complex mixture of products resulting from the polymerization of diene. However, **11** reacts with *n*-BuCs in THF with or without 18-crown-6 at –75 °C followed by silylation to give a mixture of **3** and **4** in a 3:5 ratio. Compounds **3** and **4** can be formed from anions E, F, I, and J; however, formation of I and J is less likely at –75 °C on the basis of experiments with **1** and **10** and the likelihood that metalation of **11** occurs from the more favorable trans conformer of **11** as drawn in Scheme III. The reaction of **11** under various conditions is listed in Table V. The presence of 18-crown-6 does not affect the product distribution (run 2). Evidently *n*-BuCs attacks the trans methyl group of **11** 1.6 times more readily than the cis methyl. The ratio of F to E changed to 1:3.5 on keeping the reaction mixture at –75 °C for 6 days (run 3). When the reaction mixture was warmed to room temperature for 1 h, a mixture of D–K formed, which was equilibrated in about 1 day (run 4) to give results similar to that with hydrocarbons **1** and **10**.

Reactions of *trans,trans*-2,4-Hexadiene (12). Reaction of **12** with *n*-BuCs in THF at –75 °C results in the formation of **2** in 97% selectivity on silylating the reaction mixture. This fact suggests that the hexadienyl anion formed in the reaction was either D or H or a mixture of these two. Results from the reactions of **1** and **10** under similar conditions indicate that the formation of H is less likely; also the more stable trans conformer of **12** (as drawn

Table IV. Silylation Products from Reactions of *cis*-1,4-Hexadiene (10) with Cs Solutions or with *n*-BuCs in THF

				relative mol %				
run	metalation reagent[a]	temp,[b] °C	time	2[c]	3[c]	4	5	others[d]
1	A	-75	1 h	0	0	62	32	5
2	A	-75	6 d	0	0	56	37	7
3	C	22	1 h	0	28	44	24	4
4	C	22	24 h	6	23	42	23	5
5	C	22	3 d	2	26	38	24	10
6[e]	C	22	24 h	5	48	24	16	7
		22	3 d	4	49	25	14	8

[a–e] See footnotes of Table I.

Table V. Silylation Products from Reactions of *cis,trans*-2,4-Hexadiene (11) with *n*-BuCs in THF

				relative mol %				
run	metalation reagent[a]	temp,[b] °C	time	2[c]	3[c]	4	5	others[d]
1	C	-75	2 h	0	35	55	2	8
2	D	-75	2 h	0	33	55	2	10
3	D	-75	6 d	0	20	73	0	7
4	C	22	1 h	5	32	32	21	10
		22	24 h	5	45	27	17	6
		22	5 d	6	44	27	14	9

[a–d] See footnotes of Table I.

Table VI. Silylation Products from Reactions of *trans,trans*-2,4-Hexadiene (12) with *n*-BuCs in THF

				relative mol %				
run	metalation reagent[a]	temp,[b] °C	time	2[c]	3[c]	4	5	others[d]
1	C	-75	2 h	97	0	0	0	3
2	D	-75	6 d	92	0	0	0	8
3	C	21	2 h	7	77	3	2	11
4[e]	C	21	24 h	6	59	18	12	6
		21	4 d	6	50	23	13	10

[a–e] See footnotes of Table I.

Table VII. Carbonation Products from the Reactions of Biallyl (13) with Cs Solutions in THF at -75 °C

			GC area %					
run	metalation reagent[a]	time	methyl vinylacetate	16	17	18	isomerized[b]	others[c]
1	A	40 min	3	36	38	18	0	5
2	A	6 h	9	30	41	11	4	5
3	A	11 h	7	26	51	0	16	0
4	B	40 min	*d*	31	41	16	0	12
5	B	2 h	*d*	30	37	15	3	15
6	B	8 h	1	20	35	0	38	6

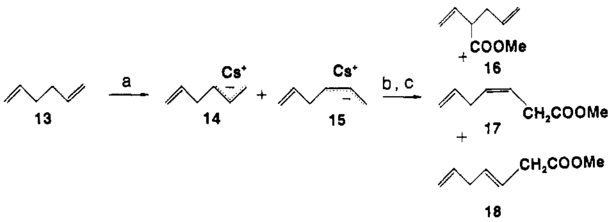
[a] Metalation reagents: A, Cs·18-crown-6 (1:1); B, Cs·18-crown-6 (2:1). [b] Isomerized product refers to conjugated hexadienyl carboxylic acids. [c] Include hexadienyl dicarboxylic acids. [d] No attempt was made to detect this.

in Scheme IV) is likely also to afford the more stable geometry for the transition state during the metalation process. The reactions of 12 with n-BuCs are summarized in Table VI. Anion D is stable at -75 °C for a long time (6 days, run 2). However, it isomerizes rapidly to F and/or J at room temperature within 1 h (run 3). On prolonged storage at room temperature in presence of a catalytic amount of n-Bu_2Hg, the reaction mixture equilibrated (run 4) to give a mixture of carbanions D–K as in the case of hydrocarbons **1**, **10**, and **11**.

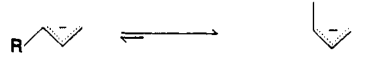
Reactions of Biallyl (13). Biallyl reacts with a 0.10–0.15 M solution of cesium metal and 18-crown-6 (1:1) in THF at -75 °C to give $(CH_2{\cdots}CH{\cdots}CH{-}CH_2CH{=}CH_2)^-Cs^+$ (Table VII). The yield of the product was 18% in 40 min (as judged by carbonation) assuming that only 1 mol of cesium is required per mole of product. On increase of the reaction time to 6 h, the yield was 79% based on Cs.

Analysis of the carbonation mixture from a 40-min reaction by GC of the methyl esters showed three monocarboxylic esters **16–18** as major products in 85 area % and seven or eight dicarboxylic esters as minor products in 10–15 area % (Scheme V). However, the carbonation mixture from an 11-h reaction showed only **16** and **17**; this result indicates that in the initial stage of the reaction the carbanion was a mixture of endo and exo forms which slowly equilibrated to the more stable endo form only. Such endo preference was previously observed by Schlosser et al.[22] for 2-alkenyl anions.

Scheme V[a]



[a] Key: (a) Cs·18-crown-6 (1:1 or 2:1), THF, -75 °C; (b) CO_2; (c) CH_2N_2.



14, exo 15, endo R = $CH_2CH{=}CH_2$

About 3–6% scission of biallyl was also observed in these reactions to give allylcesium. The percentage of dicarboxylic acids was very low in an 11-h reaction; however, 16% of the product was isomerized to give conjugated derivatives. We presume that the reaction of biallyl with cesium solution is also a two-step reaction as suggested in reaction of 1 under similar conditions. Short time reactions of biallyl with ceside solutions (excess Cs) almost doubled the yield of the product compared to electride reactions. However, when the reaction time was extended to 8 h, the yield was not as good as in electride runs. These results suggest that 18-crown-6 may be essential for the solvation of product and Cs or CsH may have precipitated out from the solution in longer duration reactions.

Compound 16 was identified by GC retention time and GC/MS which were identical to the methyl ester of the product from reaction of the dilithium salt of vinylacetic acid with allyl bromide. Compound 17 was identified by ^{1}H NMR data (obtained by subtracting the ^{1}H NMR spectrum of 16 from the mixture spectrum of 16 and 17) and MS. Identifications of 16–18 were also established using a series of conversions as described here. Compound 16 on heating undergoes Cope rearrangement to give conjugated straight chain ester 19 (mixture of cis and trans isomers). Compound 19 reacts in presence of a methanolic solution of sodium methoxide to give the methanol adduct 20. Compounds 17 and 18 also isomerize to 19 in a methanolic solution of sodium methoxide and finally give the methanol adduct 20 (eqs 4–6). Conversion of 17 and

$$16 \rightarrow \underset{19}{CH_2{=}CHCH_2CH_2CH{=}CHCOOMe} \qquad (4)$$

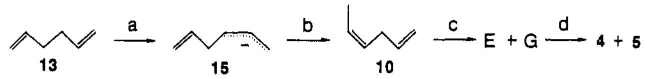
$$17 \text{ or } 18 \rightarrow 19 \qquad (5)$$

$$19 + MeOH \rightarrow \underset{20}{CH_2{=}CHCH_2CH_2CH(OMe)CH_2COOMe} \qquad (6)$$

18 to 20 confirms that they are straight chain esters with cis and trans configurations. Hydrogenation of the mixture of esters 16–18 from the reaction gave two saturated esters, methyl *n*-heptanoate and methyl 2-ethylpentanoate, which were characterized by comparing GC retention times and MS with authentic samples. The ratio of these two acids confirms that 17 and 18 are the straight chain esters.

Attempts were also made to follow the reactions of 13 by silylation. Silylation of the reaction mixtures from short period runs which still have blue color resulted in a complex mixture of products; however, long duration reactions gave a mixture of products which were identified by GC/MS and ^{1}H NMR spectroscopy. The reaction of 13 with Cs·18-crown-6 solution at −75 °C for 18 h, at which time the blue color of the reaction mixture changed to yellow-orange, on silylation gave *cis*-2,5-hexadienyltrimethylsilane (21) as the major product (44%) and 2–5 (56%). These results are in accord with carbonation experiments. Compound 21 was characterized by ^{1}H NMR spectroscopy and GC/MS data. In another experiment when the reaction time was increased to 7 days at −75 °C, only isomerized products were isolated and the composition was similar to one obtained from the reaction of 10 with Cs·18-crown-6 solution for short or longer periods at −75 °C. Formation of isomerized carbanion may be explained on the basis of either an intramolecular [1,4] sigmatropic shift of hydrogen or an intermolecular mechanism involving protonation of 13 to give *cis*-1,4-hexadiene (10), which on remetalation would give the observed products (Scheme VI). Attempted reaction of a 50:50 mixture of biallyl-3,3,4,4-d_4 ($CH_2{=}CHCD_2CD_2CH{=}CH_2$) and 13 with Cs·18-crown-6 in THF at −75 °C was carried out to elucidate the mechanism of isomerization. Silylation of the reaction mixture after 4 days at −75 °C gave hexadienyltrimethylsilanes containing 0, 1, 2, or 3 deuterium atoms, which could only be explained by an intermolecular protonation and remetalation process. An intramolecular [1,4] hydrogen shift would give only $CH_2DCH{=}CDCD{=}CHCH_2SiMe_3$ and corresponding nondeuterated silane.

Scheme VI[a]



[a] Key: (a) Cs·18-crown-6 (1:1) in THF for 7 days; (b) H$^+$; (c) metalation by Cs·18-crown-6 or 15; (d) Me_3SiCl.

Reactions of 13 with *n*-BuCs were complicated and gave poor yields of monosilylated and disilylated hexadiene derivatives.[14f]

It is worth mentioning here the results of Yasuda et al.,[11] who have reported that the reaction of biallyl, 1,4-hexadienes, or 2,4-hexadienes with potassium metal in a mixture of THF and Et_3N at 65 °C followed by silylation gave 3 in 92% yield regardless of which geometrical isomer of hexadiene was used. A similar experiment in our laboratory failed to give the claimed selectivity of the product; instead a mixture of 3 and 4 was obtained in about 80% yield (see Experimental Section) along with minor quantities of 2 and 5.

Conclusions

The present work extends that previously reported[23] concerning the unique reducing properties of Cs and Cs–K–Na alloy in THF at low temperatures. The present work reports the advantageous use of 18-crown-6 in further promoting solution of cesium metal in THF at −75 °C (a 0.11 M solution for 1:1 Cs/18-crown-6 and 0.15 M solution for 2:1 Cs/18-crown-6 are representative of the high concentrations of cesium metal dissolved in THF and utilized in the present work[24]) and facilitating its reaction with diolefins. This study of reactions of diolefins was prompted by the inability in previous work[25] of obtaining appreciable reaction of Cs–K–Na alloy with monoolefins in THF. The use of 18-crown-6 along with Cs metal (1:1 molar ratio) in THF at −75 °C gave only 2.4% yield[26] of allylic metalation products from 1-heptene in 6 h. In the present work with biallyl, rather than 1-heptene, the yield of metalation products was 79% under similar conditions. Both double bonds of biallyl therefore play a role in the fairly facile metalation of this 1,5-hexadiene by Cs·18-crown-6. In somewhat related work Schlosser[14d] has reported that 1,5-hexadiene is metalated by BuLi·KO-*t*-Bu in THF roughly 5 times faster than 1,7-octadiene or any 1-alkene (after statistical correction).

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(22) Schlosser, M.; Hartmann, J. *J. Am. Chem. Soc.* **1976**, *98*, 4674–4676 and references therein.

(23) (a) Grovenstein, E., Jr.; Longfield, T. H.; Quest, D. E. *J. Am. Chem. Soc.* **1977**, *99*, 2800–2803. (b) Grovenstein, E., Jr.; Bhatti, A. M.; Plagge, F. A.; Heinrich, Y. M.; Longfield, T. M.; Singh, J.; VanDerveer, D. *Organometallics* **1990**, *9*, 2587–2593.

(24) The molarity of the cesium solutions cited represents the amount of active cesium metal dissolved at the prevailing concentration of 18-crown-6 employed. If it is assumed that the inactive cesium (likely oxide or alkoxide) is solvated by one 18-crown-6 per cesium, then 2.0 ± 0.1 mol of cesium metal dissolves per mole *of remaining* 18-crown-6 when excess cesium metal is present; this agrees with expectations for cesium·18-crown-6 ceside in the solution.

(25) Longfield, T. H. Ph.D. Thesis, Georgia Institute of Technology, 1974.

(26) Unpublished experiments of S.C.G.

The more facile metalation of 1,4- compared to 1,5-dienes by solutions of cesium metal can be understood on the basis of greater stabilization of the product and of the transition state leading to this product when the double bonds are closer to one another and the C–H bond undergoing cleavage so that the product hexadienyl anion is fully conjugated. The question of why biallyl undergoes predominant C–H cleavage as opposed to the C–C bond cleavage (3–6% scission to allylcesium) while bibenzyl and 4-phenyl-1-butene undergo predominant C–C cleavage[27] may depend upon greater steric congestion for C–H cleavage than C–C cleavage when phenyl is present as a near substituent. More detailed explanation of these structural effects must await fuller understanding of the mechanism of C–H cleavage.

An advantage of Cs·18-crown-6 as a metalating agent is that it permits reaction at −75 °C. This temperature is sufficiently low so that allylic and pentadienylic anions have some stability in the geometrical configuration in which they are formed. Hence, cesium·18-crown-6 may occasionally offer the best route to a desired anion in a particular configuration (see the metalation of biallyl by Cs·18-crown-6 in Table VII and text).

It is difficult to understand why the initial anion from biallyl undergoes faster isomerization (trans to cis) than the initial anions from *cis*- and *trans*-1,4-hexadiene. Also the mechanism of action of n-Bu$_2$Hg in catalytically equilibrating conjugated hexadienyl anions has not been ascertained (cf. ref 18).

Finally, the present work demonstrates, in accord with prior work,[8,10,11] that the MINDO calculations of Dewar and co-workers[5] and likely other quantum mechanical calculations which ignore cation–anion interactions and solvation are not likely to yield meaningful answers to the problems of interest to the chemists who work in solvents. Thus, the exo-W anion which was estimated to be the most stable by MINDO was one of the least stable hexadienyl anions according to equilibrations of these anions as studied by silylation (Table I).

Experimental Section

trans-1,4-Hexadiene (95% pure, remainder 5% cis isomer), *cis*-1,4-hexadiene (99%), *cis,trans*-2,4-hexadiene (98%), *trans,trans*-2,4-hexadiene (99%), biallyl (98%), and 18-crown-6 were obtained from Aldrich. Biallyl-3,3,4,4-d_4 was synthesized by a literature procedure.[28] Cesium metal (99.9%) was from Callery Chemical Co. THF (Fisher) was stored over sodium wire and freshly distilled over LiAlH$_4$ under a nitrogen atmosphere directly into the Morton flask used for the organoalkali preparations. The stock solution of CsO-*t*-Bu was prepared by the reaction of cesium metal and *t*-BuOH in THF, and the molarity of the solution was determined by acid–base titration.

Gas chromatographic (GC) analyses were done on Varian 3600 and 1400 GC instruments fitted with J&W fused silica capillary column (0.252 mm × 30 M) coated with OV-1 (polydimethylsiloxane) or OV-17 (polymethylphenylsiloxane) as the stationary phase and utilized flame ionization detectors. Quantitative GC analyses were made with internal standards (benzyltrimethylsilane for silylated products and methyl heptanoate for esters) and calibrations based upon authentic samples. All yields reported here are quantitative GC yields and calculated on the basis of active Cs or n-BuCs. Qualitative GC analyses are reported as "relative mole percent" of total volatile constituents. Ratios of the isomers which are not separable under our GC conditions were determined using NMR integrations. These analyses were confirmed by relative retention times, mixed GC with authentic samples, GC/mass spectrometry (electron impact and/or chemical ionization), and NMR analyses.

^{1}H NMR spectra were recorded at fields corresponding to 300 and 400 MHz in CDCl$_3$ and reported in ppm (δ) downfield from TMS as internal standard. Mass spectra were run on a Varian MAT 112S (with SS200 data system) mass spectrometer interfaced to a Varian 3700 gas chromatograph. The capillary column used in GC/MS was a 0.252 mm × 30.0 m J&W fused silica capillary column coated with OV-1.

General Method for the Preparation of Cs·18-Crown-6 Solution and Its Reaction with Hexadienes. All reactions involving Cs metal were run in the usual Morton[29] apparatus enclosed in a glovebox under an atmosphere of N$_2$ and/or carbon dioxide from the dry ice-cooled bath to reduce fire hazards. The apparatus was thoroughly flame dried under a flow of N$_2$. A flask containing THF and LAH was attached to the condenser, and THF (as needed) was distilled into the flask. The distillation flask and condenser were then removed. Cesium metal was poured into the reaction flask and stirred for 5–6 min at room temperature to get a fine dispersion. The temperature of the reaction flask was then lowered to −75 °C using a dry ice–acetone bath with the simultaneous addition of 18-crown-6 solution in THF. Stirring was started again after about half of the 18-crown-6 solution had been added. A deep blue color solution was formed. Stirring was continued at this temperature for 1 h in the case of 1:1 solutions of Cs and 18-crown-6 and for 3–4 h in case of excess of Cs metal. The strength of the Cs·18-crown-6 solution (or amount of active Cs) was determined by the difference in the acid–base titration of the deep blue solution after decomposition with water and with chlorobenzene. The acid–base titer after decomposition first with the water gives total alkanity of the solution whereas the titer after addition of chlorobenzene gives only the amount of Cs that did not react with chlorobenzene (i.e. decomposed Cs in the form of oxide, hydroxide, or alkoxide). A 0.058 M solution of HCl for titration was used with phenolphthalein as indicator. The reported yields are based on the amount of active Cs or otherwise as stated. A solution of desired hexadiene in THF was added to the deep blue solution of Cs metal via cannula and stirred for the desired length of time and then carbonated by forcing onto crushed dry ice. For silylation the reaction mixture was quenched by adding a THF solution of Me$_3$SiCl via cannula in 5–6 min.

Extraction of Silylated Products. THF was removed from the silylated product by distillation on a steam bath through a 12-in. Vigreux column. The residue was treated with brine solution and extracted three times with n-pentane. Pentane layers were combined and dried over anhydrous MgSO$_4$. Excess of pentane was removed again by distillation on a Vigreux column to give a colorless liquid which may be further purified by vacuum distillation.

Extraction of Acidic Products. The carbonated product was neutralized with 5% HCl and saturated with NaCl. The THF layer was separated, the aqueous layer was extracted two times with 20-mL portions of Et$_2$O, and the ethereal extracts were combined with the THF layer. After drying of the extract over anhydrous MgSO$_4$, solvent was removed by distillation through a 12-in. Vigreux column on a steam bath. The residue was redissolved in 20 mL of ether and extracted three times with 5% NaOH. The alkaline layers were mixed, acidified with 5% HCl, saturated with NaCl, and again extracted with ether three times (20–30-mL portions). The ethereal layers were combined, dried over anhydrous MgSO$_4$, and concentrated to give a mixture of acids, which was converted to esters by treating with freshly prepared diazomethane.

Reactions of *trans*-1,4-Hexadiene (1) with Cs Solutions or with *n*-BuCs in THF. a. Silylation Reactions. In a typical experiment (run 1, Table I) Cs metal (2.81 g, 21.1 mmol) was dissolved in THF (150 mL) in the presence of 18-crown-6 (5.57 g, 21.1 mmol) as described above and gave a solution containing 15.7 mmol of active cesium. Compound 1 dissolved in 10 mL of THF was added via cannula in 2 min; the reaction mixture was stirred for 5 min at −75 °C whereupon the deep blue color of the solution changed to yellow-orange. The mixture was then silylated by adding rapidly Me$_3$SiCl (2.78 g, 24.8 mmol in 20 mL of THF).

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According to quantitative GC analysis the silylated product contained 1.40 g, 9.1 mmol, of hexadienyltrimethylsilanes (58%). GC relative mole % analysis: **2** and **3**, 91 (**2**, 59, and **3**, 22, by NMR); **4**, 4; **5**, 1; branched chain, 4. Since isomers **2** and **3** were not separable under our GC conditions, the percentage of **2** and **3** was determined using the $-CH_2SiMe_3$ integration ratio in ^1H NMR spectroscopy. GC/MS of **2** and **3** (together) gave *m/e* (relative intensity) 154.1 (25), 73.1 (100); for the branched chain isomer, GC/MS gave *m/e* 154.1 (7), 73.0 (100). ^1H NMR data are summarized in Table II.

Run 2 was conducted with 3.14 g (23.5/mmol) of Cs metal, 6.22 g (23.5 mmol) of 18-crown-6 (containing 15.8 mmol of active Cs), and 2.58 g (31.4 mmol) of **1** in THF (total volume 174 mL) at −75 °C exactly as run 1 except that the stirring time after the addition of **1** was extended to 1 h. Quantitative GC yield of the hexadienyltrimethylsilanes was 2.09 g (13.5 mmol), 86%.

Run 3 was conducted with a ceside solution prepared from Cs metal (3.87 g, 29.1 mmol) and 18-crown-6 (3.61 g, 13.6 mmol) in THF at −75 °C (active Cs, 17.3 mmol) and reacted with **1** (1.78 g, 21.6 mmol) similar to run 1 except the reaction time was extended to 6 h. Quantitative GC yield of the hexadienyltrimethylsilanes was 2.09 g (13.6 mmol), 78%.

Run 4 involved the reaction of **1** with *n*-BuCs. To a THF (57 mL) solution of CsO-*t*-Bu (14.5 mmol) was added **1** (1.08 g, 13.1 mmol) dissolved in 10 mL THF at −75 °C with stirring. *n*-BuLi (14.1 mmol) solution in hexane (1.4 mL) was added via syringe over 4–5 min to give a yellow-orange solution and solid product. Stirring was continued for 1 h followed by silylation (Me_3SiCl, 4.47 g, 41.1 mmol, in 20 mL of THF). The quantitative GC yield of the hexadienyltrimethylsilanes was 0.98 g, 6.3 mmol, 45%.

Run 5 was conducted with a THF (75 mL) solution of CsO-*t*-Bu (11.3 mmol), 1.15 g (14.0 mmol) of **1**, and 1.1 mL of *n*-BuLi (11.1 mmol) solution in hexane exactly as run 4. Fifteen minutes after the addition of *n*-BuLi, an 18-crown-6 (2.93 g, 11.1 mmol) solution in 20 mL of THF was added very slowly (20 min) and stirring was continued for 1 h followed by silylation (Me_3SiCl, 2.28 g, 21.1 mmol, in 20 mL of THF). The quantitative GC yield of the hexadienyltrimethylsilanes was 0.99 g, 6.4 mmol, 58%.

Run 6 was carried out using the same amount of the reactants and using exactly the same conditions as in run 4 except that 10 min after the addition of *n*-BuLi the temperature was allowed to rise to room temperature. At −35 °C all solid product was dissolved and the color of the solution changed to red. The solution was held at room temperature for 1 h and then silylated (Me_3SiCl, 4.47 g, 41.1 mmol, in 20 mL of THF). The quantitative GC yield of the hexadienyltrimethylsilanes was 1.53 g, 10.0 mmol, 71%.

Run 7 was conducted with CsO-*t*-Bu (4.8 mmol) in 25 mL of THF, **1** (0.40 g, 4.9 mmol, in 5 mL of THF), and 0.48 mL of *n*-BuLi (4.8 mmol) solution in hexane similar to run 6. The reaction mixture was kept at room temperature for 24 h and silylated (Me_3SiCl, 1.69 g, 15.5 mmol, in 10 mL of THF). The GC yield of the hexadienyltrimethylsilane was 0.19 g, 1.2 mmol, 25%.

Run 8 with CsO-*t*-Bu (15.1 mmol) in 130 mL of THF, 1.83 g (22.2 mmol) of **1** in 5 mL of THF, and 1.6 mL of solution of *n*-BuLi (16.2 mmol) in hexane was conducted exactly as in run 6. The reaction mixture was kept at room temperature for 3 days, and an aliquot A of 40 mL was withdrawn and silylated. The remaining solution was kept for 4 more days (total 7 days) and then silylated (aliquot B). Quantitative GC yield of hexadienyltrimethylsilanes: for aliquot A, 0.50 g, 3.3 mmol, 60%; for aliquot B, 0.37 g, 2.4 mmol, 25%.

Run 9 with CsO-*t*-Bu (4.0 mmol) in 20 mL of THF, 0.33 g (4.2 mmol) of **1** in 5 mL of THF, and *n*-BuLi (4.0 mmol) in hexane (0.4 mL) was conducted similar to run 6. The temperature was then lowered to −75 °C and stirred for 2 h followed by silylation (Me_3SiCl, 1.58 g, 14.5 mmol in 10 mL of THF). The quantitative GC yield of the hexadienyltrimethylsilanes was 0.18 g, 1.2 mmol, 29%.

Run 10 was conducted with 10.2 mmol of CsO-*t*-Bu in 65 mL of THF, 0.87 g (10.6 mmol) of **1**, and 0.9 mL of *n*-BuLi (9.1 mmol) in hexane similar to run 4. Temperature was then allowed to rise, and the solution was finally refluxed (65 °C) for 45 min at which time the color changed from yellow orange to brown red. The refluxing reaction mixture was then silylated by the addition of Me_3SiCl (2.24 g, 20.6 mmol in 20 mL of THF). The quantitative GC yield of the hexadienyltrimethylsilanes was 0.43 g, 2.8 mmol, 31%.

Run 11 was conducted with CsO-*t*-Bu (10.2 mmol) in 65 mL of THF, **1** (0.89 g, 10.8 mmol in 10 mL of THF), 0.9 mL of solution of *n*-BuLi (9.1 mmol) in hexane, and 2.54 g (9.6 mmol) of 18-crown-6 dissolved in 20 mL of THF exactly similar to run 5. The temperature was then allowed to rise and held at room temperature for 1 h followed by silylation (Me_3SiCl, 2.53 g, 23.3 mmol, in 20 mL of THF). The quantitative GC yield of the hexadienyltrimethylsilanes was 0.49 g, 3.2 mmol, 35%.

Run 12 with CsO-*t*-Bu (12.1 mmol) in 85 mL of THF, **1** (1.21 g, 14.7 mmol) in 10 mL of THF, and 1.3 mL of solution of *n*-BuLi (13.1 mmol) in hexane was conducted similar to run 6. Stirring was continued at room temperature for 5 h, and n-Bu_2Hg (58 mg, 0.18 mmol in 5 mL of THF) was added. An aliquot A of 40 mL was withdrawn after 24 h and silylated (Me_3SiCl, 1.21 g, 11.2 mmol in 20 mL THF). The remaining solution was kept for a total of 4 days (aliquot B) and silylated (Me_3SiCl, 1.89 g, 17.4 mmol in 20 mL of THF). Quantitative GC yield of the hexadienyltrimethylsilanes: for aliquot A, 0.48 g, 3.1 mmol, 65%; for aliquot B, 0.70 g, 4.6 mmol, 63%.

b. Hydrogen Evolution. This reaction was conducted like run 1 of Table I except that a mercury-filled gas buret was added to the usual apparatus at the point of attachment and in place of the usual inlet for nitrogen. This reaction was conducted at −75 °C with 3.20 g (24.1 mmol) of Cs metal, 6.51 g (24.6 mmol) of 18-crown-6, and 2.08 g (25.2 mmol) of **1**. The reaction mixture prior to addition of **1** contained 19.2 mmol of active cesium. Five minutes after the addition of **1** when the color of the reaction mixture had changed from blue to orange the volume of gas evolved amounted to 3.1 mmol of hydrogen (32% of theory). After addition of methanol (10 mL) and stirring for 5 min, an additional 0.74 mmol of hydrogen was evolved (this corresponds to 8% yield of CsH). These yields of hydrogen must be regarded as minimal since it is difficult to prevent small leaks of gas about the shaft of the Morton stirrer. Analysis of the reaction mixture by GC showed the presence of **1** and two hydrocarbons of longer retention time than THF (likely 2,4-hexadienes) but gave no evidence for *n*-hexane or hexenes.

c. Carbonation Reactions. To a deep blue solution of Cs·18-crown-6 containing 11.9 mmol of active Cs (prepared from 2.1 g, 15.7 mmol, of Cs and 4.1 g, 15.5 mmol, of 18-crown-6) was added **1** (1.47 g, 17.9 mmol, dissolved in 10 mL of THF) via cannula during 2 min. The reaction mixture was stirred for 5 min and forced onto solid carbon dioxide. Acid–base workup and esterification of the carbonated product gave colorless liquid (GC yield 1.02 g, 8.1 mmol, 69%). GC relative mole ‰ analysis: **6** and **7** (not separable under GC conditions used), 76; **8**, 15; **9**, 9. GC/MS [*m/e* (relative intensity): **6** and **7** (together), 140 (27), 111 (2), 98 (16), 81 (100), 80 (18), 79 (25), 77 (8), 59 (13); **8**, 140 (48), 125 (15), 109 (5), 84 (34), 81 (100), 80 (20), 79 (73), 77 (27), 59 (36); **9**, 140 (9), 125 (3), 111 (1), 108 (2), 98 (4), 81 (100), 80 (12), 79 (26), 77 (8), 59 (12). Chemical ionization MS with NH_4^+ ion showed a molecular ion peak at *m/e* 158.1 for all these isomers.

Column chromatography of the mixture of **6**–**9** (1.0 g) on silica gel (Silica Woelm 32–63, 100 g) using a 0.5% solution of diethyl ether in hexane as eluting solvent gave two fractions. First fraction (60 mg) GC analysis (%): **8**, 44; **9**, 56. Chemical shifts and coupling constants for **9** were calculated by subtracting the spectra of a synthetic sample of pure **8** from the spectrum of the first fraction. Second fraction (100 mg) GC analysis (%): **6** and **7**, 97; **8** and **9**, 3. ^1H NMR spectra of this mixture showed that the **6**:**7** ratio was 5:1. Chemical shifts and coupling constants for these isomers are summarized in Table III.

Synthesis of Methyl 2-Methyl-3,5-hexadienoate (8). To a solution of diisopropylamine (14.40 g, 121 mmol) in THF (200 mL) at −75 °C was added *n*-BuLi (101 mmol) solution in hexane (10 mL) via syringe slowly with continuous stirring. After 30 min a solution of sorbic acid (5.59 g, 50 mmol) in THF (10 mL) was added, and the dry ice–acetone bath was replaced by a wet ice–salt bath whereupon the temperature was raised to −20 °C in 30 min. Stirring was continued for another 30 min, and again the temperature was lowered to −75 °C followed by the slow addition of MeI (6.2 mL, 14.13 g, 100 mmol) diluted in THF (10 mL). The reaction mixture was stirred for 2 h, and then the temperature was raised to room temperature during 15 h. The acid was isolated by the usual acid–base extraction and esterified with diazomethane to give **8**. The yield of crude product was 5.52 g, 39.4 mmol, 79%. GC area % analysis: **8**, 88; dialkylation product, 12. Compound **8** was further purified by bulb to bulb distillation (80–85 °C/20 mm). ^{1}H NMR data are given in Table III.

Reactions of *cis*-1,4-Hexadiene (10) with Cs Solutions or with *n*-BuCs in THF. a. Silylation Reactions. The reactions of **10** under variable conditions are summarized in Table IV. In a typical experiment the Cs solution in THF (run 1) was prepared by dissolving Cs metal (2.10 g, 15.8 mmol) in 90 mL of THF in the presence of 18-crown-6 (3.88 g, 14.7 mmol) dissolved in 20 mL of THF at -75 °C by a procedure as described in an earlier part of this section. This solution contained 10.5 mmol of active Cs. Compound **10** (1.25 g, 14.7 mmol) diluted with 10 mL of THF was added via cannula whereupon the deep blue color of the solution changed to yellow-orange in 2–3 min. Stirring was continued for 1 h followed by silylation of the reaction mixture by adding Me$_3$SiCl (3.26 g, 30.0 mmol) dissolved in 20 mL of THF and worked up as usual. The quantitative GC yield of the hexadienyltrimethylsilanes was 1.25 g, 8.1 mmol, 78%. Chemical shifts and coupling constants for **4** and partial data for **5** were obtained from the 400-MHz ^{1}H NMR spectra of this mixture (Table II). GC/MS data [*m*/*e* (relative intensity)]: **4**, 154.0 (100), 139.0 (6), 81.0 (7), 73.0 (22); **5**, 154.2 (23), 139.1 (1), 73.0 (100).

Run 2 was conducted with a Cs solution containing 10.7 mmol of active Cs in 90 mL of THF (prepared from the same amount of reactants as in run 1) and **10** (1.31 g, 16.0 mmol) diluted with 10 mL of THF at -75 °C. The resulting reaction mixture was stored at -75 °C for 6 days and then silylated (Me$_3$SiCl, 2.16 g, 19.9 mmol, in 20 mL of THF). The quantitative GC yield of the hexadienyltrimethylsilanes was 0.83 g, 5.4 mmol, 50%.

Run 3 involved the reaction of **10** with *n*-BuCs. Hexadiene **10** (0.69 g, 8.4 mmol) diluted with 10 mL of THF was added to CsO-*t*-Bu (7.8 mmol) solution in THF (65 mL) at -75 °C with stirring. *n*-BuLi (8.1 mmol) solution in hexane (0.8 mL) was added slowly via syringe. The reaction mixture was allowed to warm and held at room temperature for 1 h followed by silylation (Me$_3$SiCl, 1.62 g, 14.9 mmol, in 20 mL of THF). The quantitative GC yield of the hexadienyltrimethylsilanes was 0.67 g, 4.3 mmol, 55%.

Run 4 was carried out with CsO-*t*-Bu (4.1 mmol) in THF (25 mL), **10** (0.31 g, 3.8 mmol) in 10 mL of THF, and *n*-BuLi (4.0 mmol) in hexane (0.4 mL) exactly similar to run 3. The reaction mixture was kept at room temperature for 24 h and silylated (Me$_3$SiCl, 1.42 g, 13.1 mmol, in 10 mL of THF). The quantitative GC yield of the hexadienyltrimethylsilanes was 0.32 g, 2.0 mmol, 53%.

Run 5 with **10** (0.61 g, 7.4 mmol in 10 mL of THF), CsO-*t*-Bu (5.5 mmol in 30 mL of THF), and *n*-BuLi (5.5 mmol) in hexane (0.5 mL) was conducted similar to run 3. The reaction mixture was stored at room temperature for 3 days and then silylated (Me$_3$SiCl, 1.62 g, 14.9 mmol in 10 mL of THF). The quantitative GC yield of the hexadienyltrimethylsilanes was 0.53 g, 3.4 mmol, 62%.

Run 6 was carried out with **10** (1.30 g, 15.8 mmol, in 10 mL of THF), CsO-*t*-Bu (10.6 mmol in 75 mL of THF), and *n*-BuLi (12.1 mmol) in hexane (1.2 mL) exactly similar to run 3. After 5 h of stirring at room temperature, *n*-Bu$_2$Hg (0.048 g, 0.15 mmol) diluted with 5 mL of THF was added and held at room temperature. An aliquot A of 30 mL was withdrawn after 24 h and silylated (Me$_3$SiCl, 1.62 g, 14.9 mmol, in 10 mL THF). The remaining 60 mL of solution (aliquot B) was kept for another 2 days and silylated (Me$_3$SiCl, 1.62 g, 14.9 mmol in 10 mL of THF). Quantitative GC yield of the hexadienyltrimethylsilanes: for aliquot A, 0.21 g, 1.3 mmol, 38%; for aliquot B, 0.44 g, 2.8 mmol, 40%.

b. Carbonation Reactions. To a solution containing 11.3 mmol of active Cs (prepared from Cs metal, 2.56 g, 19.26 mmol, and 18-crown-6, 5.00 g, 18.91 mmol, at -75 °C in 90 mL of THF) was added **10** (0.95 g, 11.5 mmol) diluted with 10 mL of THF over 2 min whereupon the color of the reaction mixture was changed to yellow-orange. The reaction mixture was carbonated after 1 h by forcing it on solid dry ice. Acid–base workup and esterification of carbonated product gave a colorless liquid (yield of esters 0.55 g, 3.9 mmol, 35%). GC relative mole % analysis: unknown 1, 23; **8**, 32; unknown 2, 45. Unknown 1 is likely to be *cis*-CH$_3$CH=CHCH(COOMe)CH=CH$_2$ (see ref 20). No attempt was made to identify unknown 2, which would likely be straight chain isomers of hexadienoic acids.

Reactions of *cis*,*trans*-2,4-Hexadiene (11) with *n*-BuCs in THF. Reactions of **11** under variable conditions are summarized in Table V. In a typical experiment (run 1) **11** (0.75 g, 19.1 mmol) diluted with 10 mL of THF was added to a solution of CsO-*t*-Bu (6.0 mmol) in THF (45 mL) at -75 °C with stirring. A solution of *n*-BuLi (7.1 mmol) in hexane (0.7 mL) was added slowly. The color of solution turned yellow, and some yellow solid was deposited in 4–5 min. Stirring was continued for 2 h at -75 °C, and the reaction mixture was then silylated by adding Me$_3$SiCl (1.33 g, 12.3 mmol) solution in 10 mL of THF. According to quantitative GC, the yield of the hexadienyltrimethylsilanes was 0.75 g, 4.91 mmol, 81%. ^{1}H NMR spectroscopy confirms the absence of **2**, and chemical shifts and coupling constants for the major isomers correspond to **3** and **4**.

Run 2 was conducted with CsO-*t*-Bu (6.0 mmol) in 45 mL of THF, **11** (0.75 g, 4.91 mmol) diluted with 10 mL of THF, and *n*-BuLi (7.1 mmol) solution in hexane (0.7 mL) similar to run 1 followed by the slow addition of 18-crown-6 (1.61 g, 6.1 mmol) dissolved in 10 mL of THF, and the temperature was maintained at -75 °C. After 2 h of stirring, the reaction mixture was silylated by adding Me$_3$SiCl (1.23 g, 11.3 mmol, in 10 mL of THF). The quantitative GC yield of the hexadienyltrimethylsilanes was 0.70 g, 4.6 mmol, 76%.

Run 3 with CsO-*t*-Bu (6.0 mmol) in 50 mL of THF, **11** (0.97 g, 11.8 mmol) in 10 mL of THF, *n*-BuLi (7.1 mmol) in hexane (0.7 mL), and 18-crown-6 (1.65 g, 6.2 mmol) was conducted exactly as in run 2, and the reaction mixture was then stored at -75 °C for 6 days before silylation (Me$_3$SiCl, 1.82 g, 16.8 mmol, in 10 mL of THF). The quantitative GC yield for the hexadienetrimethylsilanes was 0.18 g, 1.2 mmol, 20%.

Run 4 was started with CsO-*t*-Bu (12.0 mmol) in 80 mL of THF, **11** (1.66 g, 20.2 mmol) diluted with 10 mL of THF, and 1.3 mL of *n*-BuLi (13.1 mmol) in hexane similar to run 1. After the addition of *n*-BuLi was completed, the reaction mixture was allowed to warm and held at room temperature. An aliquot A of 30 mL was withdrawn after 1 h and silylated (Me$_3$SiCl, 1.00 g, 9.2 mmol, in 10 mL of THF). Another aliquot B of 30 mL was withdrawn after 24 h and silylated (Me$_3$SiCl, 1.00 g, 9.2 mmol, in 10 mL of THF). The remaining solution aliquot C (30 mL) was kept for 5 days and silylated (Me$_3$SiCl, 1.00 g, 9.2 mmol, in 10 mL of THF). Quantitative GC yield of the hexadienyltrimethylsilanes: for aliquot A, 0.34 g, 2.2 mmol, 56%; for aliquot B, 0.26 g, 1.7 mmol, 43%; for aliquot C, 0.19 g, 1.2 mmol, 31%.

Reactions of *trans*,*trans*-2,4-Hexadiene (12) with *n*-BuCs in THF. In a typical experiment (run 1, Table VI) a solution of **12** (1.04 g, 12.7 mmol) in THF (10 mL) was added to CsO-*t*-Bu (10.0 mmol) in 70 mL of THF at -75 °C with stirring. *n*-BuLi (10.1 mmol) solution in hexane (1.0 mL) was added slowly whereupon a yellow solid product deposited within 2 min. Stirring was continued at -75 °C for 2 h before silylation (Me$_3$SiCl, 2.78 g, 25.7 mmol, in 10 mL of THF). The quantitative GC yield of the hexadienyltrimethylsilanes was 0.75 g, 4.8 mmol, 48%.

Run 2 with CsO-*t*-Bu (10.3 mmol) in 70 mL of THF, **12** (1.13 g, 13.7 mmol) diluted with 10 mL of THF, and *n*-BuLi (11.1 mmol) solution in hexane (1.1 mL) was carried out similar to run 1. After the addition of *n*-BuLi, 18-crown-6 (2.68 g, 10.2 mmol) solution in THF (20 mL) was added slowly over 30 min. The reaction mixture was kept at -75 °C for 6 days prior to silylation (Me$_3$SiCl, 2.52 g, 23.2 mmol, in 10 mL of THF). The quantitative GC yield for the hexadienyltrimethylsilanes was 0.60 g, 3.9 mmol, 38%.

Run 3 was conducted with CsO-*t*-Bu (5.0 mmol) in 40 mL of THF, **12** (0.54 g, 6.6 mmol) in 10 mL of THF, and *n*-BuLi (6.1 mmol) solution in hexane (0.6 mL) similar to run 1. After 30 min, the reaction mixture was warmed up slowly and held at room temperature for 2 h (color of solution became orange-yellow) and then silylated (Me$_3$SiCl, 1.21 g, 11.2 mmol, in 10 mL of THF). The quantitative GC yield of the hexadienyltrimethylsilanes was 0.52 g, 3.4 mmol, 68%.

Run 4 was carried out using CsO-*t*-Bu (12.1 mmol) in 90 mL of THF, **12** (1.27 g, 15.4 mmol) in 10 mL of THF, and *n*-BuLi (13.1 mmol) solution in hexane (1.3 mL) exactly similar to run 3. After 5 h of stirring, *n*-Bu$_2$Hg (0.101 g, 0.32 mmol) diluted with 5 mL of THF was added, and the reaction mixture was held at room temperature. An aliquot A of 40 mL was withdrawn after 24 h and silylated (Me_3SiCl, 1.00 g, 9.2 mmol in 10 mL of THF). Remaining solution aliquot B (65 mL) was kept for 3 more days and silylated (Me_3SiCl, 1.00 g, 9.2 mmol in 10 mL of THF). Quantitative GC yield of the hexadienyltrimethylsilanes: for aliquot A, 0.23 g, 1.5 mmol, 33%; for aliquot B, 0.62 g, 4.0 mmol, 54%.

Reactions of Biallyl (13) with Cs Solutions in THF in the Presence of 18-Crown-6 at −75 °C. In a typical procedure (run 1, Table VII) to a deep blue solution of Cs·18-crown-6 containing 16.1 mmol of active Cs (prepared from 2.9 g, 22.1 mmol of Cs; 5.68 g, 21.5 mmol of 18-crown-6 in 150 mL of THF) was added an excess of biallyl (3.63 g, 44.2 mmol) at −75 °C. The reaction mixture was stirred for 40 min, during which time the color of the solution remained deep blue. The reaction mixture was carbonated by forcing it over crushed dry ice. GC area % analysis of methyl esters: methyl vinylacetate, 3; **16**, 36; **17**, 38; **18**, 18; others (others include esters of monomerdicarboxylic acids; 7–8 isomers present; each having molecular ion (M^+) peak in GC/MS at *m/e* 198), 5. Quantitative GC yield: **16**–**18**, 0.42 g, 3.0 mmol, 19%; methyl vinylacetate, 0.017 g, 0.17 mmol, 3% scission of total biallyl reacted. GC/MS data [*m/e* (relative intensity)]: **16**, 140 (1), 125 (5), 111 (11), 99 (30), 81 (100), 80 (61); **17**, 140 (4), 125 (2), 111 (5), 109 (8), 108 (3), 98 (26), 81 (100), 80 (61); **18**, 140 (4), 125 (1), 111 (4), 109 (3), 108 (3), 98 (20), 81 (100), 80 (68); methyl vinylacetate, 100 (52), 72 (21), 69 (33), 59 (85), 58 (22), 41 (100).

Run 2 was carried out by using Cs·18-crown-6 solution containing 17.9 mmol of active Cs (prepared from 2.91 g, 21.9 mmol, of Cs and 5.70 g, 21.6 mmol, of 18-crown-6 in 160 mL of THF) and **13** (3.53 g, 21.6 mmol) diluted with 10 mL of THF at −75 °C similar to run 1. The reaction mixture was stirred for 6 h and then carbonated. Quantitative GC yield: **16**–**18**, 0.96 g, 7.6 mmol, 43%; methyl vinylacetate, 0.10 g, 1.0 mmol, 6% scission of total biallyl reacted.

Run 3 was conducted with Cs·18-crown-6 solution containing 23.9 mmol of active Cs (prepared from 3.99 g, 30.0 mmol, of Cs and 7.64 g, 28.9 mmol, of 18-crown-6 in 210 mL of THF) and **13** (4.79 g, 58.4 mmol) diluted with 10 mL of THF similar to run 1. The reaction mixture was stirred for 11 h, at which time color of the solution became light green, and then carbonated. Quantitative GC yield: **16** and **17**, 1.80 g, 12.9 mmol, 54%; isomerized products, 0.52 g, 3.7 mmol, 15%; methyl vinylacetate, 0.22 g, 2.2 mmol, 6% scission of total biallyl reacted. The mixture of esters was distilled by the bubble tube technique (100–110 °C/20 mm), and the 400-MHz ^1H NMR spectrum was recorded. The chemical shifts and coupling constants for **17** were obtained by subtracting spectra of **16** (prepared by another route) from the spectra of this mixture and summarized in Table III.

Run 4 involved the reaction of Cs·18-crown-6 solution containing 14.7 mmol of active Cs (prepared by using excess Cs, 4.37 g, 32.8 mmol, and 18-crown-6, 4.31 g, 16.3 mmol, in 100 mL of THF) and **13** (2.82 g, 34.1 mmol) exactly similar to run 1 for 40 min. Quantitative GC yield: **16**–**18**, 0.54 g, 3.9 mmol, 27%.

Run 5 with Cs·18-crown-6 solution containing 20.8 mmol of active Cs (prepared from excess Cs, 4.97 g, 37.4 mmol, and 18-crown-6, 4.15 g, 15.7 mmol, in 170 mL of THF) and **13** (6.18 g, 75.1 mmol) diluted with 10 mL of THF was conducted similar to run 1, and the reaction mixture was stirred for 2 h followed by carbonation. Quantitative GC yield: **16**–**18**, 1.03 g, 8.2 mmol, 39%.

Run 6 was conducted with Cs·18-crown-6 solution containing 13.4 mmol of active Cs (prepared from excess Cs, 3.42 g, 25.7 mmol, and 18-crown-6, 3.02 g, 11.4 mmol, in 130 mL of THF) and **13** (4.52 g, 55.0 mmol) diluted with 10 mL of THF similar to run 1 and stirred for 8 h. The reaction mixture was then carbonated to give 1.01 g, 8.0 mmol, 60%, of a mixture of crude acids.

Preparation of Methyl 2-Vinyl-4-pentenoate (16). To a solution of lithium diisopropylamide in 400 mL of THF at −75 °C (prepared from *n*-BuLi, 202 mmol, in 20 mL of hexane and 24.23 g, 240 mmol, of diisopropylamine) was added vinylacetic acid (8.77 g, 102 mmol) dissolved in 10 mL of THF slowly via syringe. The dry ice–acetone bath was replaced by an ice–salt bath, and the temperature was allowed to rise to −20 °C in 30 min and held for another 30 min. The temperature was again lowered to −75 °C, and allyl bromide (28.7 g, 237 mmol) solution in 10 mL of THF was added via dropping funnel with stirring. The reaction mixture was warmed up again to −5 °C for 18 h, and finally the usual acid–base separation gave 13.8 g of crude acid, which was converted to methyl ester by reaction with diazomethane. GC area % analysis: **16**, 87; other isomer, 12; dialkylation product, 1 (confirmed by GC/MS). Ester **16** was further purified by distillation using a Hickman distillation apparatus (bath temperature 60–70 °C/20 mm). ^1H NMR data are summarized in Table III. The exact mass of **16** by high-resolution MS: calcd, *m/e* 140.0837; found, *m/e* 140.0825.

Cope Rearrangement of the Mixture of 16–18 Obtained from Biallyl and Then Base-Catalyzed Addition of Methanol. (i) A mixture of **16**–**18** obtained from the reaction of biallyl with Cs·18-crown-6 at −75 °C for 40 min as in run 1 (1.22 g) (GC area % analysis: **16**, 16; **17**, 59; **18**, 24) was heated at 190 °C under a N_2 atmosphere for 18 h to isomerize **16** to **19** by Cope rearrangement. GC area % analysis after rearrangement: **16**, 1; **17**, 54; **18**, 25; **19** (trans), 18; **19** (cis), 2. GC/MS for **19** (trans) [*m/e* (relative intensities)]: 140 (2), 125 (3), 111 (13), 109 (28), 108 (20), 99 (12), 81 (93), 80 (76), 41 (100).

(ii) To 1.10 g of the mixture from part i in MeOH (10 mL) was added NaOMe (8.5 mmol) in 8.5 mL of MeOH, and the solution was stirred at room temperature for 48 h under N_2. The reaction mixture was then treated with HCl and saturated with NaCl and extracted three times with ether (20 mL each). The ethereal layers were combined, dried over anhydrous $MgSO_4$, and concentrated on a rotatory evaporator to give 0.85 g, 4.9 mmol, of **20** in more than 90% purity by GC area % analysis. The crude product was distilled by the bubble tube technique (80–90 °C bath/20 mm). ^1H NMR data (300 MHz, $CDCl_3$) ($H_2{}^aC{=}CH^xCH_2{}^bCH_2{}^cCH^d$-($OMe^e$)$CH^fH^{f'}COOMe^g$): δ 5.79 (ddt, $J_{ax(trans)} = 17.0$, $J_{ax(cis)} = 10.3$ and $J_{bx} = 6.6$ Hz, H^x, 1 H), 5.03 (complex, d, $H^a{}_{trans}$, 1 H), 4.97 (complex d, $H^b{}_{cis}$, 1 H), 3.69 (s, H^g, 3 H), 3.65 (complex m partly under H^g, H^d), 3.35 (s, H^e, 3 H), 2.56 (dd, $J = 15.1$ and 7.1 Hz, $H^{f\text{ or }f'}$, 1 H), 2.42 (dd, $J = 15.1$ and 5.5 Hz, $H^{f\text{ or }f'}$, 1 H), 2.13 (complex m, H^b, 2 H), 1.62 (complex m, H^c, 2 H). GC/MS [*m/e*, (relative intensity)]: 157 (2), 140 (17), 130 (8), 117 (14), 109 (7), 99 (13), 98 (7), 81 (20), 75 (100). Exact mass of **20** determined by CI for MH^+: calcd, *m/e* 173.1178; obsd, *m/e* 173.1185.

Cope Rearrangement of Synthetic 16 to 19 Followed by Base-Catalyzed Addition of Methanol To Give 20. (i) Compound **16** (2.42 g, 17.3 mmol) was heated at 190 °C for 36 h under N_2. GC area % analysis: **19** (trans), 93; **19** (cis), 7. GC retention time and GC/MS of the major product were identical to that obtained from isomerization of the biallyl reaction product (previous experiment). ^1H NMR (300 MHz) data for **19** (trans) are summarized in Table III. Exact mass of **19** (trans) by CI: calcd, *m/e* 140.0837; obsd, *m/e* 140.0862.

(ii) Compound **19** (1.47 g, 10.5 mmol) and NaOMe (10.5 mmol) were reacted in MeOH (10 mL) for 48 h under N_2 at room temperature, and **20** was isolated as described earlier in 83% GC analysis. ^1H NMR spectra and GC/MS were similar to the product isolated from isomerization of the biallyl product.

Hydrogenation of a Mixture of 16–18 Obtained from the Reaction of Biallyl and Cs·18-Crown-6 for 40 min. A mixture of **16**–**18** (0.133 g, 0.95 mmol), prepared as in run 1, was hydrogenated in MeOH (10 mL) in the presence of 0.05 g of PtO_2 as catalyst. GC area % analysis: methyl *n*-heptanoate, 64; methyl 2-ethylpentanoate, 36. GC/MS of these esters was similar to authentic samples.

Reaction of Biallyl (13) with Cs·18-Crown-6 in THF at −75 °C for 18 h Followed by Silylation. To a solution containing 4.1 mmol of active Cs (prepared from 1.19 g, 8.9 mmol, of Cs and 2.52 g, 9.5 mmol, of 18-crown-6 in 115 mL of THF at −75 °C) was added **17** (1.70 g, 20.7 mmol) diluted with 10 mL of THF with stirring. After a few hours stirring the solution was transferred to a 250-mL flask and stored at −75 °C for 18 h followed by silylation (Me_3SiCl, 2.29 g, 21.0 mmol, in 10 mL of THF). GC yield of the hexadienyltrimethylsilanes was 0.29 g, 1.9 mmol, 45%. GC relative mole % analysis: **21**, 44; **2** and **3**, 10; **4**, 32; **5**, 13. The product was distilled by the bubble tube technique, and 400-MHz ^1H NMR data for **21** are summarized in Table II. GC/MS for **21** [*m/e* (relative intensity)]: 154 (5), 139 (12), 111 (4), 80 (8), 74 (12), 73 (100).

Reaction of Biallyl (13) with Cs·18-Crown-6 Solution in THF at −75 °C for 7 Days Followed by Silylation. Hexadiene **13** (4.04 g, 49.2 mmol) dissolved in 10 mL of THF was added to a solution containing 22.2 mmol of active Cs (prepared from 3.93 g, 29.5 mmol, of Cs and 7.89 g, 29.8 mmol, of 18-crown-6 in 200 mL of THF at −75 °C), and the reaction mixture was stored in −75 °C for 7 days followed by silylation (Me_3SiCl, 10.2 g, 85.8 mmol, in 20 mL of THF). The GC yield of the hexadienyltrimethylsilanes was 1.40 g, 9.1 mmol, 41%. GC relative mole % analysis: **2** and **3**, 10; **4**, 67; **5**, 22; a trace of unisomerized products. GC/MS and ^1H NMR spectra of the major product were similar to those of **4** obtained from the reactions of **10**.

Reaction of a Mixture of Biallyl-3,3,4,4-*d*$_4$ and 13 with Cs·18-Crown-6 Solution in THF at −75 °C. A 50:50 mixture of biallyl-3,3,4,4-d_4 (1.11 g, 12.9 mmol) and **13** (1.12 g, 13.7 mmol) dissolved in 10 mL of THF was added to a Cs·18-crown-6 solution containing 14.0 mmol of active Cs (prepared from 2.61 g, 19.6 mmol, of Cs and 4.33 g, 16.4 mmol, of 18-crown-6 in 120 mL of THF at −75 °C), and the reaction mixture was kept for 4 days at −75 °C before silylation (Me_3SiCl, 5.10 g, 42.8 mmol, in 20 mL of THF). The GC yield of hexadienyltrimethylsilanes was 0.42 g, 2.7 mmol, 19%. GC relative mole % analysis: **2**, 18: **4**, 38; **5**, 34; branched chain, 5; unisomerized material, 5. High-resolution MS for isotopic ratio [m/e of M^+ (relative %)]: **2**, 154.1178 (58.7), 155.1241 (12.8), 156.1303 (18.7), 157.1366 (8.3) and 158.1400 (1.5); **4**, 154.1178 (45.4), 155.1241 (13.1), 156.1303 (22.9), 157.1366 (15.8), 158.1400 (2.8); **5**, 154.1178 (48.3), 155.1241 (13.0), 156.1303 (22.6), 157.1366 (13.6), 158.1400 (2.4). The molecular ion peaks at m/e 154, 155, 156, 157, and 158 corresponds to isomers having 0–4 deuterium atoms. These values are not corrected for the isotopic abundance of carbon.

Preparation of CsH. To Cs metal (1.75 g, 12.9 mmol) suspended in hexane (10 mL) was added *t*-BuOH (0.86 g, 11.7 mmol) diluted with 10 mL of hexane with stirring. After 1 h a H_2 atmosphere was established in the reaction flask and the temperature was lowered to −20 °C. Tetramethylethylenediamine (1.28 g, 11.0 mmol) solution in 5 mL of hexane was added and the temperature lowered to −40 °C. *n*-BuLi (10.6 mmol) in 10 mL of hexane was added dropwise via dropping funnel. The temperature of the reaction mixture was then raised to 5 °C with a H_2 atmosphere maintained. After 1 h of stirring when all *n*-BuLi had reacted (tested with Watson and Eastham[30] indicator) CsH was ready to use. To determine the % yield of CsH, the temperature of the reaction mixture was lowered to −75 °C and 1–2 mL of MeOH was added. The volume of the liberated H_2 gas was 159.3 mL at STP (7.1 mmol), which amounts to 67% yield of CsH based on *n*-BuLi.

Reactions of CsH with 1 and 13 in the Presence of 18-Crown-6 in THF at −75 °C. CsH was prepared as described in the previous experiment using 1.87 g, 14.04 mmol, of Cs metal and then allowed to react with **1** (0.66 g, 8.03 mmol, diluted with 20 mL of THF). There was no visible color change. 18-Crown-6 (2.03 g, 7.86 mmol) dissolved in 50 mL of THF was added slowly whereupon the reaction mixture turned yellow-orange. Stirring was continued for 1 h, and then the reaction mixture was carbonated. The GC yield of mixture of esters was 0.22 g, 1.8 mmol, 22% based on the amount of **1**.

A similar experiment with CsH prepared from 2.32 g, 17.5 mmol, of Cs metal and **13** (1.42 g, 17.3 mmol) was carried out in presence of 18-crown-6 (3.26 g, 12.3 mmol) to give a mixture of esters (0.09 g, 0.7 mmol, 4% based on amount of **13**).

Reaction of 13 with Potassium in THF at 65 °C in the Presence of Triethylamine. Potassium sand (1.90 g, 48.6 mmol) was prepared in a boiling mixture of THF (60 mL) and Et_3N (30 mL) in a Morton flask using a high-speed stainless-steel mechanical stirrer. Biallyl (8.26 g, 100.5 mmol) diluted with 10 mL of THF was added and refluxed for 3 h with stirring. The solution was then transferred to a 250-mL flask, and organopotassium compound was precipitated by adding dry hexane. The supernatant liquid was removed via cannula, and the residue was washed two times with hexane (5 mL each) to give a red solid. The red compound was redissolved in THF (50 mL) and divided into two parts. The first part was silylated by adding an excess of Me_3SiCl (5.0 g, 46.0 mmol) dissolved in 20 mL of THF at −40 °C. From the second portion, organopotassium compound was precipitated again by adding hexane, and the suspension of the product was silylated (Me_3SiCl, 5.0 g, 46.0 mmol) at 0 °C with stirring. GC area % analysis showed that the composition of silylated product from both portions within experimental error was the same. The GC yield of the hexadienyltrimethylsilanes was 2.18 g, 14.2 mmol, 29% based on K. GC area % analysis: **2** and **3**, 55 (**2**, 5, and **3**, 50, by NMR); **4**, 30; **5**, 5; branched chain, 10.

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