Registry No. $W(CCMe_3)NP_3$, 68490-69-7; $W(CCMe_3)(OCMe_3)_3$, 78234-36-3; $W(CCMe_3)(NMe_2)_3$, 82209-29-8; $W(CCMe_3)(SCMe_3)_3$, 83416-64-2; $[W(CCMe_3)(OMe)_3(NMe_2H)]_2$, 83416-65-3; $[PEt_3H][W(CCMe_3)Cl_4]$, 83416-67-5; $[NEt_4][W(CCMe_3)Cl_4]$, 78251-20-4; $[NEt_4][W(CCMe_3(PEt_3)Cl_4]$, 83416-69-7; $W(CCMe_3)(dme)Cl_3$, 83416-70-0; $W(CCMe_3)(Et_3PO)Cl_3$, 78251-21-5; $W(CCMe_3)(Et_3PO)(PEt_3)Cl_3$, 78481-48-8; $W(CCMe_3)(PMe_3)_3Cl_3$, 78251-18-0; $W(CCMe_3)(PMe_3)_2Cl_3$, 83461-72-7; $W(CCMe_3)(PMe_3)Cl_3$, 83416-71-1; $W(CCMe_3)(PEt_3)Cl_3$, 82661-16-3; $W(CCMe_3)(N\text{-}i\text{-}Pr_2)_3$, 82810-47-7.

A Useful Dienemethylation Agent: 2,4-Pentadienyltrimethylsilane[†]

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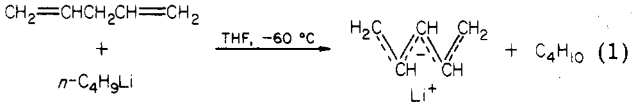
(*E*)- or (*Z*)-2,4-pentadienyltrimethylsilane reacts with aldehydes and ketones in dichloromethane solution in the presence of $TiCl_4$ to give, after hydrolysis, alcohols of type $RCH(OH)CH_2CH{=}CHCH{=}CH_2$ and $RR'C(OH)CH_2CH{=}CHCH{=}CH_2$, respectively (*E* isomer only), in generally good yield. Experiments with (*Z*,*E*)-2,4-hexadienyltrimethylsilane showed that an S_E2' process is operative, since with aldehydes the products were of the type $RCH(OH)CH(CH_3)CH{=}CHCH{=}CH_2$. $Me_3SiCH_2CH{=}CHCH{=}CH_2$ also reacted with acetals and ketals to replace an alkoxy group with $CH_2CH{=}CHCH{=}CH_2$.

Introduction

In principle, pentadienyllithium, 1, whose preparation and structure in solution was reported by Bates and his co-workers in 1967 (eq 1),[2] should be a useful reagent for



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the introduction of the $CH_2{=}CHCH{=}CHCH_2$ group into diverse organic structures by standard organolithium methodology. In practise, this is not the case since pentadienyllithium reacts with aldehydes[3] and ketones[4] to give, after hydrolysis, a mixture of isomeric alcohols, as shown in eq 2 and 3, in which the new C–C bonds have been

$$Li(CH_2CHCHCHCH_2) + C_2H_5CH{=}O \xrightarrow{\text{THF, 20 °C}} \xrightarrow{H_2O} \underset{\text{31 parts}}{(CH_2{=}CH)_2CHCH(OH)C_2H_5} + \underset{\text{69 parts}}{CH_2{=}CHCH{=}CHCH_2CH(OH)C_2H_5} \quad (2)$$

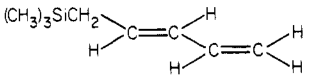
$$Li(CH_2CHCHCHCH_2) + (C_2H_5)_2C{=}O \xrightarrow{\text{THF, 20 °C}} \xrightarrow{H_2O} \underset{\text{44 parts}}{(CH_2{=}CH)_2CHC(OH)(C_2H_5)_2} + \underset{\text{56 parts}}{CH_2{=}CHCH{=}CHCH_2C(OH)(C_2H_5)_2} \quad (3)$$

formed at the central as well as at the terminal carbon atoms of the reagent. The addition of 1 to the C=O bond of aliphatic aldehydes was found to be irreversible, but reversibility could be demonstrated in the case of the reaction of 1 with ketones. Thus, when the THF solution of the lithium alkoxide mixture formed in some (but not all) of the 1/ketone reactions was heated at 60 °C for 5 h, the isomer mixture was converted to a single isomer, the dienylmethyl alkoxide $CH_2{=}CHCH{=}CHCH_2CR_2OLi$.[4] For instance, such was found to be the case in the 3-pentanone reaction.

It seemed to us that a reagent which could add the pentadienyl group to the C=O bond of aldehydes and ketones under mild conditions to give exclusively products of type $RR'C(OH)CH_2CH{=}CHCH{=}CH_2$ would be a useful addition to the arsenal of the synthetic organic chemist. We have found such a reagent in 2,4-pentadienyltrimethylsilane, $(CH_3)_3SiCH_2CH{=}CHCH{=}CH_2$.

Results and Discussion

In contrast to the C=O additions of pentadienyllithium, the reaction of this reagent with trimethylchlorosilane was regiospecific, giving only (*E*)-2,4-pentadienyltrimethylsilane, 2, in high yield. This compound is, in a sense, an



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allylic silane, and as such it possibly could react with aldehydes and ketones in the presence of a Lewis acid (as do allylsilanes: eq 4[5]). In the case of 2, we are dealing

$$R_3SiCH_2CH{=}\overset{*}{C}H_2 + {>}C{=}O \xrightarrow{\text{Lewis acid}} \xrightarrow{\text{hydrolysis}} {>}C(OH)\overset{*}{C}H_2CH{=}CH_2 \quad (4)$$

with a conjugated system, so that it might be expected that its reaction with an organic carbonyl compound would take the course shown in eq 5.

$$(CH_3)_3SiCH_2CH{=}CHCH{=}\overset{*}{C}H_2 + {>}C{=}O \xrightarrow{\text{Lewis acid}} \xrightarrow{\text{hydrolysis}} {>}C(OH)\overset{*}{C}H_2CH{=}CHCH{=}CH_2 \quad (5)$$

[†] Dedicated to the memory of Rolly Pettit, a friend and a brilliant and imaginative chemist.

(1) NATO Postdoctoral Fellow at the Massachusetts Institute of Technology, 1979–1980; on leave from the Laboratoire de Synthese Organique, Université de Poitiers.

(2) Bates, R. W.; Gosselink, D. W.; Kaczynski, J. A. *Tetrahedron Lett.* **1967**, *199*, 205.

(3) Gerard, F.; Miginiac, P. *Bull. Soc. Chim. Fr.* **1974**, 1924.

(4) Gerard, F.; Miginiac, P. *Bull. Soc. Chim. Fr.* **1974**, 2527.

(5) (a) Mangravite, J. A. *J. Organomet. Chem. Libr.* **1979**, *7*, 45. (b) Rubottom, G. *Ibid.* **1979**, *8*, 322 (and earlier Annual Surveys of "Silicon:Applications to Organic Synthesis").

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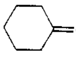
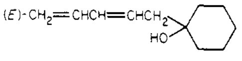
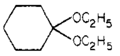
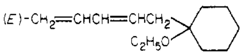
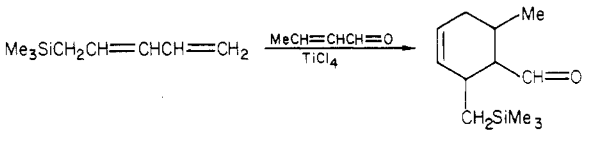
Table I. $TiCl_4$-Induced Reactions of 2,4-Pentadienyltrimethylsilane with Aldehydes, Ketones, Acetals, and Ketals

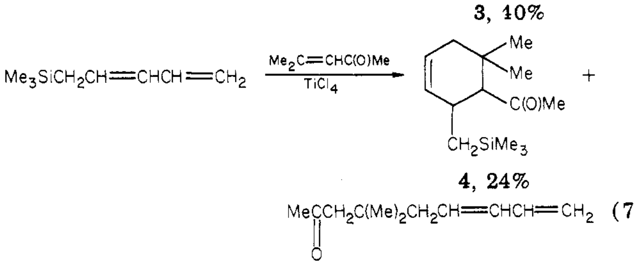
substrate	product (% yield)
$C_2H_5CH{=}O$	(*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C_2H_5$ (79)
n-$C_3H_7CH{=}O$	(*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C_3H_7$-*n* (70)
$(CH_3)_2CHCH{=}O$	(*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)CH(CH_3)_2$ (80)
n-$C_4H_9CH{=}O$	(*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C_4H_9$-*n* (80)
$(CH_3)_3CCH{=}O$	(*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C(CH_3)_3$ (60)
n-$C_5H_{11}CH{=}O$	(*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C_5H_{11}$-*n* (56)
c-$C_6H_{11}CH{=}O$	(*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C_6H_{11}$-c (58)
$C_6H_5CH{=}O$	(*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C_6H_5$ (51)
$(CH_3)_2C{=}O$	(*E*)-$CH_2{=}CHCH{=}CHCH_2C(OH)C(CH_3)_2$ (48)
$(C_2H_5)_2C{=}O$	(*E*)-$CH_2{=}CHCH{=}CHCH_2C(OH)(C_2H_5)_2$ (55)
$(n\text{-}C_3H_7)_2C{=}O$	(*E*)-$CH_2{=}CHCH{=}CHCH_2C(OH)(n\text{-}C_3H_7)_2$ (80)
$CH_3C(O)CH(CH_3)_2$	(*E*)-$CH_2{=}CHCH{=}CHCH_2C(OH)(CH_3)CH(CH_3)_2$ (51)
$CH_3C(O)CH_2CH(CH_3)_2$	(*E*)-$CH_2{=}CHCH{=}CHCH_2C(OH)(CH_3)CH_2CH(CH_3)_2$ (60)
	 (64)
$(CH_3)_2CHCH_2CH(OC_2H_5)_2$	(*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OC_2H_5)CH_2CH(CH_3)_2$ (65)
$C_6H_5CH(OCH_3)_2$	(*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OCH_3)C_6H_5$ (79)
$(CH_3)_2C(OCH_3)_2$	(*E*)-$CH_2{=}CHCH{=}CHCH_2C(OCH_3)(CH_3)_2$ (46)
	 (40)

Subsequent experiments confirmed these ideas. The best results were obtained when titanium tetrachloride was the Lewis acid used and when the reactions were carried out in dichloromethane at −40 °C. In practice, the aldehyde was dissolved in dichloromethane; the resulting solution (under argon) was cooled to −40 °C and the $TiCl_4$ was added. Subsequently, the pentadienylsilane was added, and the reaction mixture was stirred while it was allowed to warm to 5 °C. When that temperature was reached, the mixture was poured into saturated aqueous sodium bicarbonate solution. In the case of the **2**/ketone reactions, it was found best to mix the ketone and $TiCl_4$ in dichloromethane solution at −40 °C and then to add the pentadienylsilane when the solution was warmed to room temperature. The results shown in Table I were obtained by using these procedures. The 250-MHz proton NMR spectra obtained for some but not all of these products showed the *E* isomer to be present. The yields have not been optimized, but at this point they are satisfactory.

The pentadienylsilane procedure does not appear to be applicable to the pentadienylation of α,β-unsaturated aldehydes and ketones, according to the two examples examined. Crotonaldehyde reacted to form a cyclic product (eq 6), while mesityl oxide reacted with (*E*)-2,4-pentadienyltrimethylsilane to give the Michael-type adduct as well as a cyclic product (eq 7). The possible mechanism of formation of the cyclic products will be discussed later.



3, 10%



4, 24%

$$\underset{\overset{\|}{O}}{MeC}CH_2C(Me)_2CH_2CH{=}CHCH{=}CH_2 \quad (7)$$

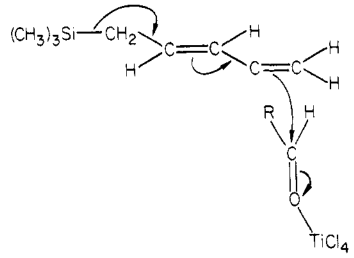
35%

2,4-Pentadienyltrimethylsilane also reacts with acetals and ketals to give the expected ethers (eq 8 and 9; also Table I). In these reactions also, only a single isomer was obtained.

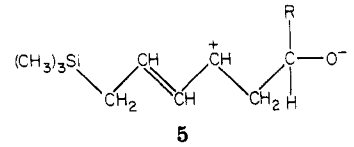
$$(CH_3)_3SiCH_2CH{=}CHCH{=}CH_2 + PhCH(OCH_3)_2 \xrightarrow[CH_2Cl_2]{TiCl_4,\ -78\ °C} \xrightarrow{\text{hydrolysis}} PhC(OCH_3)HCH_2CH{=}CHCH{=}CH_2 \quad (8)$$

$$(CH_3)_3SiCH_2CH{=}CHCH{=}CH_2 + (CH_3)_2C(OCH_3)_2 \xrightarrow[CH_2Cl_2]{TiCl_4,\ -78\ °C} \xrightarrow{\text{hydrolysis}} (CH_3)_2C(OCH_3)CH_2CH{=}CHCH{=}CH_2 \quad (9)$$

With the preparative utility of 2,4-pentadienyltrimethylsilane demonstrated by the experiments summarized in Table I, we turned our attention to the mechanism of the pentadienylation reaction. As indicated in eq 5, our working hypothesis was that the pentadienyl group transfer from silicon to carbon should proceed with pentadienyl transposition:



An intermediate carbonium ion of type **5** might be discussed as being involved in the pentadienyl-transfer reaction. This species is an allylic carbonium ion which is more properly written as **6** to show the allylic delocalization



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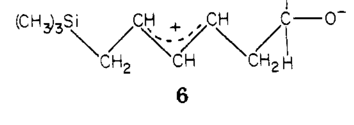

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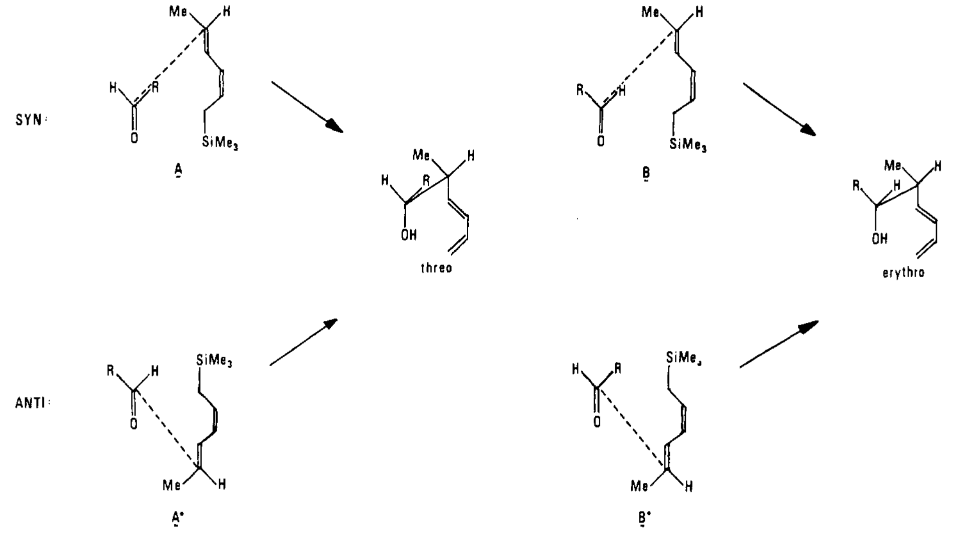
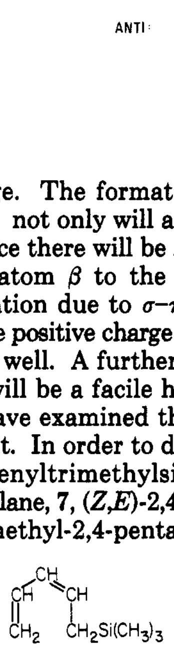
Scheme I



of charge. The formation of **6** should be especially favorable: not only will allylic stabilization be gained, but also, since there will be significant positive charge on the carbon atom β to the trimethylsilyl group, additional stabilization due to σ–π conjugation[6] may be expected. Thus the positive charge will be delocalized onto the silicon atom as well. A further consequence of such σ–π conjugation will be a facile heterolysis of the Si–C bond.

We have examined the question of mechanism by experiment. In order to do this, we prepared several other pentadienyltrimethylsilanes: (*Z*)-2,4-pentadienyltrimethylsilane, **7**, (*Z,E*)-2,4-hexadienyltrimethylsilane, **8**, and (*E*)-(4-methyl-2,4-pentadienyl)trimethylsilane, **9**.



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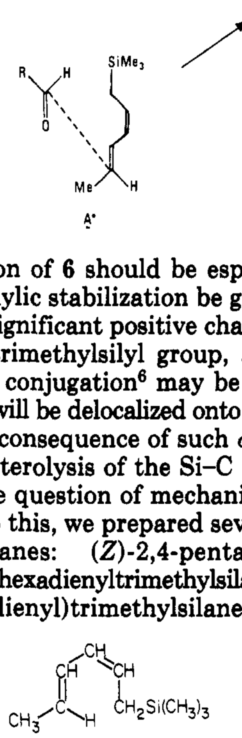

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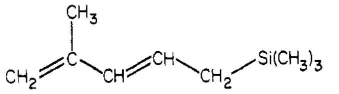

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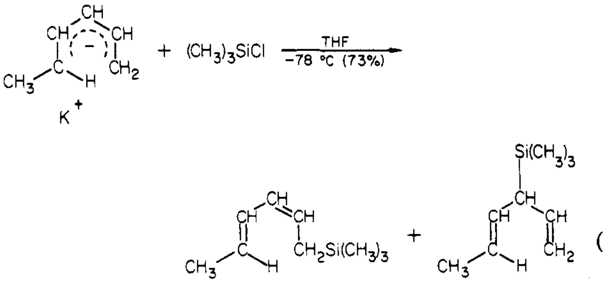
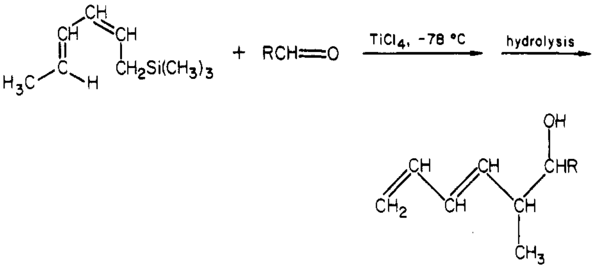
(*Z*)-2,4-Pentadienyltrimethylsilane was prepared by the procedure of Yasuda, Yamauchi, and Nakamura,[7] who had found that pentadienylpotassium in THF solution reacts with trimethylchlorosilane to give the *Z* rather than the *E* isomer as the exclusive product. The reaction of (1-methylpentadienyl)potassium [(1–5-η-hexadienyl)potassium] in THF at −78 °C with trimethylchlorosilane, we found, gives two isomeric products (eq 10), of which the major one is the desired (*Z,E*)-2,4-hexadienyltrimethylsilane. Finally, (*E*)-(4-methyl-2,4-pentadienyl)trimethylsilane was prepared (as the sole product) by the reaction of (2-methylpentadienyl)lithium with trimethylchlorosilane.



(10)

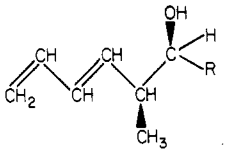
9 parts 1 part

The reactions of (*Z*)-2,4-pentadienyltrimethylsilane with two aliphatic aldehydes in the presence of titanium tetrachloride provided immediate evidence in favor of intermediate **6** in which the original geometric configuration of the 1,3-diene system is not preserved: the products in both cases were the *E* isomers of the expected alcohols (Table I). In similar reactions of (*Z,E*)-2,4-hexadienyltrimethylsilane with three aliphatic aldehydes, the alcohols formed were the *E* isomers of the products of complete pentadienyl transposition, and thus the reaction is of the S_E2' type (eq 11). The alcohols **10** were isolated as a mixture of diastereomers, **11**/**12**, in which the erythro isomer, **11**, predominates.

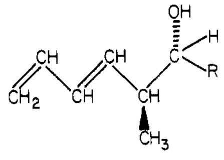


(11)

10



11



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The approach of (*Z,E*)-2,4-hexadienyltrimethylsilane and the aldehyde may be pictured as shown in Scheme I. Of the four transition states, A, A*, B, and B*, A* and B* would involve fewer nonbonded interactions of the $(CH_3)_3Si$ substituent and so should be favored. Methyl/R group repulsions should favor formation of the erythro isomer over the threo isomer, with the erythro/threo ratio decreasing with decreasing size of the R group of the aldehyde. This is what was observed. In the $TiCl_4$-induced reaction of (*Z,E*)-2,4-hexadienyltrimethylsilane with ac-

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(6) Traylor, T. G.; Berwin, H. J.; Jerkunica, J.; Hall, M. L. *Pure Appl. Chem.* **1972**, *30*, 599.

(7) Yasuda, H.; Yamauchi, M.; Nakamura, A. *J. Organomet. Chem.* **1980**, *202*, C1.

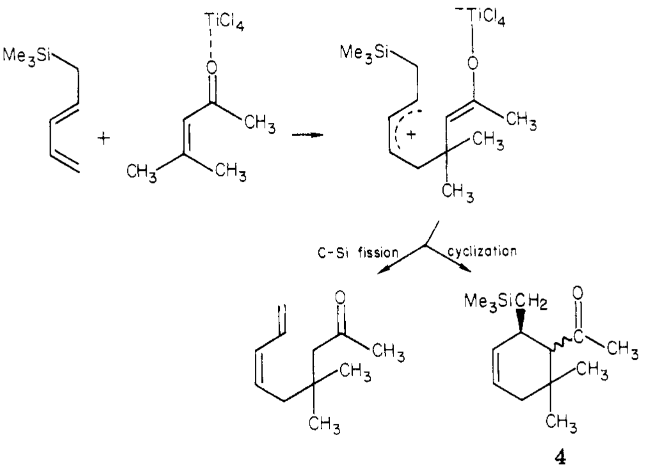
etaldehyde the erythro/threo product ratio (**11**/**12**, R = CH_3, eq 11) was 66:34; with propionaldehyde (R = C_2H_5) it was 74:26; with isobutyraldehyde (R = Me_2CH) it was 84:16.

The Lewis acid induced reaction of pentadienylsilanes with carbonyl compounds thus appears to provide yet another example of the operation of σ–π conjugation in organosilicon chemistry. It also is of interest since it is an example of an S_E2'-type process involving a homodienyl system. Finally, it provides a one-step, good yield synthesis of homoallylic dienols, $RR'C(OH)CH_2CH{=}CHCH{=}CH_2$, which the synthetic chemist will find suitable for Diels–Alder reactions.

After our preliminary communication of this work,[8] Oppolzer, Burford, and Marazza[9] reported the synthesis of 2,4-pentadienyltrimethylsilane by the organolithium route and described its conversion to (α-(trimethylsilyl)-pentadienyl)lithium by deprotonation with lithium dialkylamides. Later in 1980, Hosomi, Saito, and Sakurai[10] reported the preparation of 2,4-pentadienyl- and 2,4-hexadienyltrimethylsilane by the organopotassium in THF route, but they did not specify the stereochemistry of the products. Both reagents were shown to react with benzaldehyde in the presence of boron trifluoride diethyl etherate, with pentadienyl transposition in the case of the hexadienylsilane. Product stereochemistry was not determined. Examples of Lewis acid induced reaction of these silanes with acetals (as shown in eq 8) also were reported. (Our results on such reactions also had been communicated earlier.[11])

Finally, we return to the formation of cyclized products in the case of α,β-unsaturated carbonyl compounds (as in eq 6 and 7). The nature of the regio- and stereochemistry of the cyclic products, **3** and **4**, is important to the overall mechanism presented here. Each product was obtained as a mixture of diastereomers (by 270-MHz proton NMR), and, in the case of **4**, solely the regioisomer shown was obtained. The assignment of regiochemistry is based on literature precedent as well as on the ^1H NMR spectra. It is known that *trans*-piperylene reacts with methyl acrylate in the absence of a Lewis acid to produce a 90:10 mixture of "1,2 vs. 1,3" regioisomers. In the presence of aluminum chloride this ratio is increased to 97:3.[12] The high-field proton NMR spectra of **3** and **4** are complicated by the presence of diastereomers. This is readily apparent by the presence of two distinct aldehyde resonances in the spectrum of **3** and by the presence of two pairs of methyl singlets for the ring methyls in the spectrum of **4**. The ^1H NMR spectra of both compounds show at least two distinct Me_3Si resonances, separated by 5.4 and 3.0 Hz, respectively, for **3** and **4**. (The presence of smaller amounts ($\ll$5%) of other regioisomers cannot be excluded, however.) In the case of **3**, the diastereomer ratio could be determined to be 3:1 by integration of the aldehyde proton resonances. This is unusual in that the ratio obtained with *trans*-piperylene was 95:5.[12] It may be that in our case it is not a concerted, Lewis acid induced Diels–Alder reaction which is taking place but rather a polar, stepwise process as shown in Scheme II. Here the Me_3Si group stabilizes the β-allylic carbonium ion and C–Si bond heterolysis competes with cyclization. With this type of a process, a thermodynamic mixture of products is obtained, not the kinetic mixture expected from a concerted pathway.

Scheme II



Experimental Section

General Comments. All reactions were performed under an atmosphere of dry nitrogen or argon in flame-dried glassware. All solvents were rigorously dried before use. Infrared spectra were obtained by using a Perkin-Elmer 457A grating infrared spectrophotometer and proton NMR spectra by using a Bruker WM-250 or WM-270 or a JEOL FX-90Q spectrometer operating at 250, 270, and 90 MHz, respectively. Proton chemical shifts are reported in δ units, parts per million downfield from internal tetramethylsilane; $CDCl_3$ was used as a solvent and an internal lock and $CHCl_3$ as an internal standard (δ 7.24). Gas–liquid chromatography (GLC) was used extensively in this work in the analysis of reaction mixtures, determination of yields (by the internal standard method) and isolation of pure products for analysis and spectroscopy. Commercial F&M 700, 720, and 5754 gas chromatographs were used. GLC columns were either a 6-ft SE-30 silicone rubber gum on Chromosorb P or a 6-ft Carbowax 20M on Chromosorb W.

Dienes were purchased from Chemical Samples Co., trimethylchlorosilane from Petrarch Systems Inc. 1,4-Pentadiene was prepared by the reaction of vinylmagnesium bromide with allyl bromide.[13] Aldehydes were distilled and stored at 0 °C under nitrogen. Titanium tetrachloride was distilled at atmospheric pressure and stored at −35 °C. Potassium *tert*-butoxide (Callery Chemical Co.) was sublimed (150 °C (0.1 mmHg)) and stored in a dessicator.

Preparation of Pentadienylsilanes. All reactions were carried out in three-necked, round-bottomed flasks of appropriate size that were equipped with a magnetic stir-bar, a nitrogen inlet tube, and a pressure-equalizing addition funnel.

(1) 2,4-Pentadienyltrimethylsilane (*E* Isomer). To a solution of 21 mL of 2.45 M *n*-butyllithium in hexane (51 mmol) diluted with 50 mL of THF at −78 °C was added 5.3 mL (51 mmol) of 1,4-pentadiene over a 5-min period. The low-temperature bath was removed, and the mixture was stirred for 30 min. The resulting red solution was cooled to 0 °C and 6.5 mL, (51 mmol) of trimethylchlorosilane was added over a 5-min period. The reaction mixture was stirred at room temperature for 2 h and subsequently was hydrolyzed with 25 mL of saturated aqueous ammonium chloride. The aqueous phase was extracted with 50 mL of diethyl ether, and the combined organic phases were washed with 25 mL of saturated aqueous NaCl and dried over anhydrous $MgSO_4$. The organic layer was concentrated at reduced pressure. Distillation of the liquid residue gave 5.95 g (0.043 mol, 85%) of (*E*)-2,4-pentadienyltrimethylsilane, **2**: bp 41 °C (36 mmHg); $n^{20}{}_D$ 1.4590; IR (neat liquid) 3100 (m), 3010 (m), 2980 (s), 2900 (s), 1645 (s), 1600 (w), 1250 (vs), 870–840 (br, vs) cm^{-1}; ^1H NMR (250 MHz) δ 0.00 (s, $SiMe_3$), 1.51 (d, H_f, J_{ef} = 8.8 Hz), 4.84 (dd, H_a, J_{ab} = 1.84, J_{ac} = 10.3 Hz), 4.98 (dd, H_b, J_{ab} = 1.84, J_{bc} = 16.9 Hz), 5.69 (dt, H_e, J_{de} = 15.1, J_{ef} = 8.8 Hz), 5.91 (dd, H_d, J_{cd} = 10.3, J_{de} = 15.1 Hz), 6.28 (ddd, H_c, J_{cd} = 10.3, J_{ac} = 10.3, J_{bc} = 16.9 Hz). Anal.

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[8] Seyferth, D.; Pornet, J. *J. Org. Chem.* **1980**, *45*, 1722.

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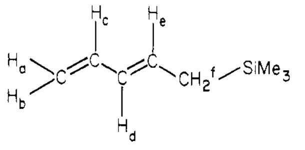
[10] Hosomi, A.; Saito, M.; Sakurai, H. *Tetrahedron Lett.* **1980**, *21*, 3783.

[11] Pornet, J. *Tetrahedron Lett.* **1980**, *21*, 2049.

[12] Inukai, T.; Kojima, T. *J. Org. Chem.* **1967**, *32*, 869.

[13] Normant, H. *C. R. Hebd. Seances Acad. Sci.* **1954**, *239*, 1510.

Calcd for $C_8H_{16}Si$: C, 68.48; H, 11.49. Found: C, 68.38; H, 11.43.

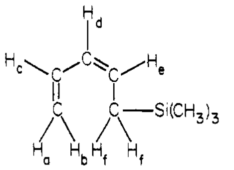


2

A similar reaction in which the pentadienyllithium reagent was treated with dimethylchlorosilane, $(CH_3)_2SiHCl$, gave 2,4-pentadienyldimethylsilane, $(CH_3)_2HSiCH_2CH{=}CHCH{=}CH_2$ (probably the *E* isomer): bp 39 °C (39 mmHg); n^{30}_{D} 1.4603; 62% yield; IR (film) ν(Si–H) 2130 cm^{-1}; ^{1}H NMR (60 MHz) δ 0.10 (d, J = 3 Hz, 6 H, Me_2Si), 1.50–1.70 (m, 2 H, CH_2), 3.70–4.10 (m, 1 H, Si–H), 4.70–6.50 (m, 5 H, diene H). Anal. Calcd for $C_7H_{14}Si$: C, 66.58; H, 11.17. Found: C, 66.96; H, 11.36.

(2) 2,4-Pentadienyltrimethylsilane (*Z* Isomer). This compound was prepared by the reaction of pentadienylpotassium, prepared by the method of Bahl, Bates, and Gordon,[14] with trimethylchlorosilane.

To a suspension of 11.1 g (0.10 mol) of potassium *tert*-butoxide in 125 mL of pentane was added 42 mL of 2.44 M *n*-butyllithium in hexane (0.10 mol) over a 5-min period. The resulting solution was stirred at room temperature for 30 min, at which time a solution of 10 mL (0.10 mol) of 1,3-pentadiene (mixed isomers) (alternatively, 1,4-pentadiene may also be used) in 100 mL of pentane was added over a 30-min period. The reaction mixture was stirred for another hour. The orange solid which had formed was allowed to settle, and the supernatant liquid was removed by cannula. Dry argon was passed over the solid for 45 min and then it was dried at 25 °C (0.1 mmHg) for 3 h. (This procedure ensures that the potassium reagent is practically pentane free.) The pentadienylpotassium thus prepared was dissolved in 375 mL of dry THF and the solution added, at –78 °C, to a solution of 13.3 mL (0.105 mol) of trimethylchlorosilane in 50 mL of THF with vigorous stirring (a mechanical stirrer was used in this case). After the addition had been completed, the reaction mixture was warmed to room temperature and stirred for 3 h. Subsequently, it was treated with 100 mL of saturated aqueous NH_4Cl. The subsequent workup followed the procedure given in (1). Distillation afforded 4.62 g (33%) of (*Z*)-2,4-pentadienyltrimethylsilane, 7: bp 44–45 °C (40 mmHg); n^{20}_{D} 1.4549; mass spectrum, *m/e* (relative intensity) M^+ 140 (9.02), $(M - 15)^+$ 125 (2.31), Me_3Si^+ 73 (100%), as well as others; ^{1}H NMR (250 MHz) δ 0.00 (s, $SiMe_3$), 1.64 (d, H_f, J_{ef} = 9.9 Hz), 5.00 (dd, H_a, J_{ab} = 1.84, J_{ac} = 10.3 Hz), 5.11 (dd, H_b, J_{ab} = 1.84, J_{bc} = 16.9 Hz), 5.49 (dt, H_e, J_{de} = 10.3, J_{ef} = 9.9 Hz), 5.92 (dd, H_d, J_{cd} = 10.2, J_{de} = 10.3 Hz), 6.57 (ddd, H_c, J_{ac} = 10.3, J_{bc} = 16.9, J_{cd} = 10.2 Hz). Anal. Calcd for $C_8H_{16}Si$: C, 68.48; H, 11.49. Found: C, 68.40; H, 11.39.



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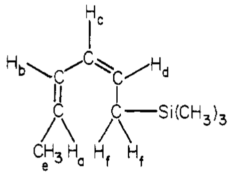
(3) (*Z*,*E*)-2,4-Hexadienyltrimethylsilane. (1-Methylpentadienyl)potassium was prepared by the reaction between 10.3 mL (90 mmol) of 2,4-hexadiene (mixed isomers) (1,4-hexadiene also may be used) and the potassium *tert*-butoxide/*n*-butyllithium reagent (from 90 mmol of *n*-BuLi in hexane) by using the procedure described for the preparation of pentadienylpotassium. The solid (1-methylpentadienyl)potassium that was formed was dissolved in 375 mL of THF, and this solution was added, at –78 °C, to a solution of trimethylchlorosilane (13 mL, 100 mmol) in 50 mL of THF. The reaction mixture was stirred for 3 h at room temperature and then was treated with saturated aqueous NH_4Cl. Workup as in the experiment above gave 10.1 g (73%) of (*Z*,*E*)-2,4-hexadienyltrimethylsilane, 8: bp 66–67 °C (20 mmHg); n^{20}_{D} 1.4689; mass spectrum (inter alia), *m/e* (relative intensity) M^+ 154, Me_3Si^+ 73 (100); ^{1}H NMR (250 MHz) δ 0.00 (s, $SiMe_3$), 1.59 (d, 2 H, H_f, J_{df} = 8.8 Hz), 1.75 (dd, 3 H, H_e, J_{ae} = 6.6, J_{be} = 1.1 Hz), 5.34 (dt, H_d, J_{cd} = 11.0, J_{df} = 8.8 Hz), 5.60 (dq, H_a, J_{ab} = 14.7, J_{ae} = 6.6 Hz), 5.89 (dd, H_c, J_{bc} = 11.1, J_{cd} = 11.0 Hz), 6.24 (ddq, H_b, J_{bc} = 11.1, J_{ab} = 14.7, J_{be} = 1.1 Hz). Anal. Calcd for $C_9H_{18}Si$: C, 70.04; H, 11.75. Found: C, 70.03; H, 11.76.



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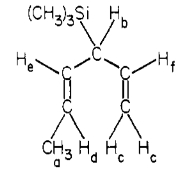
A small amount of another isomer was isolated from the distillate by preparative GLC (4-ft SE 30 on Chromosorb P, 110 °C) and identified on the basis of its IR and 250-MHz proton NMR spectra as (*E*)-3-(2,5-hexadienyl)trimethylsilane, 13: δ –0.04 (s, $SiMe_3$), 1.65 (d, 3 H, H_a, J_{da} = 7.0 Hz), 2.36 (t, H_b, J_{be} = J_{bf} = 8.5 Hz), 4.8–4.9 (m, 2 H, H_c), 5.31 (dq, 1 H, H_d, J_{ad} = 7.0, J_{de} = 15.1 Hz), 5.81 (ddd, 1 H, H_f, J = 8.5, 11.0, 16.9 Hz), 5.45 (dd, 1 H, H_e, J_{be} = 8.5, J_{de} = 15.1 Hz). The isomer ratio, 8/13, was 9.



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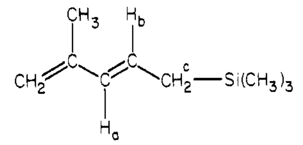
(4) (4-Methyl-2,4-pentadienyl)trimethylsilane. To a 50-mL three-necked, round-bottomed flask containing 11.8 mL of 2.45 M *n*-BuLi in hexane (29 mmol) diluted with 5 mL of THF was added at –78 °C 2.51 g (31 mmol) of 2-methyl-1,4-pentadiene over a 1-h period. The low-temperature bath was removed, and the reaction mixture was stirred at room temperature for 3 h. The resulting red solution was cooled to 0 °C, and 3.9 mL (31 mmol) of trimethylchlorosilane was added over a 5-min period. The reaction mixture was stirred at room temperature for 30 min and then was hydrolyzed with 15 mL of saturated aqueous NH_4Cl. Further workup (as in the experiments above) gave (*E*)-(4-methyl-2,4-pentadienyl)trimethylsilane: bp 52–54 °C (16 mmHg); n^{20}_{D} 1.4620; 3.12 g (70%), as the sole product; ^{1}H NMR (90 MHz, in $CDCl_3$) δ 0.00 (s, $Si(CH_3)_3$), 1.57 (d, H_c, J_{bc} = 7.8 Hz), 1.81 (s, CH_3), 4.76 (s, 2 H, $H_2C{=}$), 5.63 (dt, H_b, J_{bc} = 7.8, J_{ab} = 15.6 Hz), 6.00 (d, H_a, J_{ab} = 15.6 Hz). Anal. Calcd for $C_9H_{18}Si$: C, 70.04; H, 11.75. Found: C, 70.15; H, 11.84.



9

Structure Assignment. High-field proton NMR spectroscopy was the sole means used to assign the stereochemistry of the pentadienylsilanes. The vinylic region in the NMR spectra is very complex, but it is analyzable in terms of one stereoisomer in each case. Vicinal trans coupling is greater than cis coupling[15] and thus knowing J_{de} was of importance. In the *E* isomer of $Me_3SiCH_2CH{=}CHCH{=}CH_2$ H_d appears as a doublet of doublets centered at δ 5.91. Thus J_{cd} and J_{de} were readily identified at 10.3 and 15.1 Hz, respectively. In the case of the *Z* isomer, H_d appears in the proton NMR spectrum as a triplet, indicating that $J_{dc} \sim J_{de}$. Decoupling of the allylic protons caused H_e to collapse to a doublet with J_{de} = 10.3 Hz. These values are close to those observed[16] for the (*E*)- and (*Z*)-crotylsilanes, $CH_3CH{=}CHCH_2SiMe_3$, and this serves to assign unambiguously the

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[14] Bahl, J. J.; Bates, R. B.; Gordon, B. *J. Org. Chem.* **1979**, *44*, 2290.

[15] Günther, H. "NMR Spectroscopy"; Wiley: New York, 1980; Chapter IV.

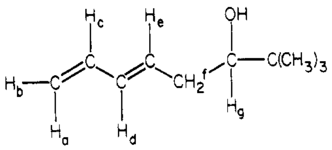
[16] $^3J_{\mathrm{trans}}$ = 15.5 Hz for (*E*)-crotyltrimethylsilane and $^3J_{\mathrm{cis}}$ = 12.0 Hz for the *Z* isomer: Sakurai, H.; Kudo, Y.; Miyoshi, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1433.

stereochemistry of the (*E*)- and (*Z*)-2,4-pentadienyltrimethylsilanes. For (*Z,E*)-2,4-hexadienyltrimethylsilane the stereochemistry about the C=C bonds was assignable only by decoupling the appropriate allyl group and observing the vinylic portion of the spectrum.

Reactions of (*E*)- and (*Z*)-2,4-Pentadienyltrimethylsilane with Aldehydes. The following general procedure was used. The reactions were carried out in a 50-mL three-necked flask equipped with a magnetic stir-bar, a no-air stopper, and a low-temperature thermometer. A solution of the aldehyde (6 mmol) in dry dichloromethane (6 mL) was prepared (under nitrogen or argon) and cooled to −40 to −60 °C, and 2 mmol of distilled titanium tetrachloride was added by syringe. This mixture then was stirred while it was allowed to warm to −20 to −10 °C and then was cooled to −55 °C. The pentadienyltrimethylsilane (4 mmol) was added, and the low-temperature bath was removed. The reaction mixture was stirred for about 10 min while it warmed to 0–5 °C. It was subsequently hydrolyzed by the addition of 10 mL of saturated aqueous $NaHCO_3$ (or by pouring into 25 mL of saturated $NaHCO_3$). The resulting mixture was extracted with three 30-mL portions of diethyl ether. The organic phase was dried over anhydrous K_2CO_3 and evaporated at reduced pressure. Trap-to-trap distillation into a receiver cooled with liquid nitrogen gave crude product. Pure samples were isolated by gas chromatography, usually by using a column containing 10% Carbowax 20M on Chromosorb W.

The following alcohols were prepared previously by the organolithium route by Gerard and Miginiac:[3] $C_2H_5CH(OH)R$, n-$C_3H_7CH(OH)R$, $(CH_3)_2CHCH(OH)R$, n-$C_6H_{13}CH(OH)R$, and $C_6H_5CH(OH)R$ (R = (*E*)-$CH_2CH{=}CHCH{=}CH_2$). The measured spectra agreed with the spectra reported by these authors. The following alcohols are new compounds: n-$C_4H_9CH(OH)CH_2CH{=}CHCH{=}CH_2$, $n^{26}{}_D$ 1.4752 (Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 76.72; H, 11.78.) (See below); $(CH_3)_3CCH(OH)CH_2CH{=}CHCH{=}CH_2$, $n^{26}{}_D$ 1.4750 (Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.51; H, 11.66.); c-$C_6H_{11}CH(OH)CH_2CH{=}CHCH{=}CH_2$, $n^{25}{}_D$ 1.5060 (Anal. Calcd. for $C_{12}H_{20}O$: C, 79.95; H, 11.18. Found: C, 79.55; H, 11.10.).

The 250-MHz proton NMR spectra were obtained for some, but not all, of the alcohols prepared in this manner. All showed that the *E* isomers had been formed. The NMR spectrum of $(CH_3)_3CCH(OH)CH_2CH{=}CHCH{=}CH_2$ (in $CDCl_3$) is typical: δ 0.92 (s, $(CH_3)_3C$), 1.60 (s, OH), 1.9–2.3 (m, 2 H, H_f), 3.26 (m, H_g), 5.0 (dd, H_b, J_{ab} = 1.5, J_{bc} = 10.3 Hz), 5.2 (dd, H_a, J_{ab} = 1.5, J_{ac} = 18.1 Hz), 5.75 (m, H_e), 6.2 (dd, H_d, J_{de} = 14.7, J_{cd} = 10.3 Hz), 6.4 (ddd, H_c, J_{bc} = 10.3, J_{ac} = 18.1 Hz).



Here also, the key feature is $J_{de} \approx 15$ Hz, indicative of trans substitution about the C=C bond in question. (Note J_{de} is 15.1 Hz in the case of (*E*)-$Me_3SiCH_2CH{=}CHCH{=}CH_2$ and 10.3 Hz in the case of the *Z* isomer.) For n-$C_4H_9CH(OH)CH_2CH{=}CHCH{=}CH_2$ J_{de} = 15 Hz; for $C_2H_5CH(OH)CH_2CH{=}CHCH{=}CH_2$, J_{de} = 14.8 Hz.

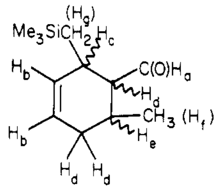
A satisfactory analysis could not be obtained for n-$C_4H_9CH(OH)CH_2CH{=}CHCH{=}CH_2$ and so it was converted to the trimethylsilyl derivative, n-$C_4H_9CH(OSiMe_3)CH_2CH{=}CHCH{=}CH_2$, by reaction with hexamethyldisilazane in the presence of a catalytic amount of Me_3SiCl: ^1H NMR (270 MHz, $CDCl_3$) δ 0.08 (s, 9 H, $SiMe_3$), 0.87 (t, J = 7.3 Hz, CH_3 of Bu, 3 H), 1.22–1.53 (br m, 6 H, $CH_2CH_2CH_2$ of Bu), 2.20 (t, $J_{ef} \approx J_{fg}$ = 7.7 Hz, 2 H, $CH_2CH{=}$), 3.63 (approximate quintet, 1 H, H_g, with J = 7.7, 5.5 Hz), 4.95 (d, J_{bc} = 10.03 Hz, 1 H, H_b), 5.08 (d, J_{ac} = 17.14 Hz, 1 H, H_a), 5.66 (dt, J_{ef} = 7.65 Hz, 1 , H_e), 6.03 (dd, J_{de} = 14.71 Hz, 1 H, H_d), 6.30 (ddd, J_{cd} = 10.35 Hz, 1 H, H_c) (proton designations as in the *tert*-butyl analogue above). Anal. Calcd for $C_{13}H_{26}OSi$: C, 68.96; H, 11.57. Found: C, 68.96; H, 11.40.

The reactions with (*Z*)-2,4-pentadienyltrimethylsilane with propionaldehyde and pivaldehyde were carried out similarly. The IR and proton NMR spectra of the products were identical with those of the products obtained by using (*E*)-2,4-pentadienyltrimethylsilane. Thus, to a solution of propionaldehyde (6 mmol) in 6 mL of dry CH_2Cl_2 was added, at −40 °C, 2.0 mmol of $TiCl_4$. The solution was stirred under nitrogen for 5 min at −40 °C and then was allowed to warm to room temperature during 10 min. It was cooled again to −45 °C, and the pentadienylsilane (4.0 mmol) was added in one portion. The reaction mixture was allowed to warm slowly to room temperature, stirred for 5 min, and treated with 10 mL of saturated aqueous sodium bicarbonate. Workup as in the experiment above gave a trap-to-trap distillate that contained (by GLC) the expected $CH_2{=}CHCH{=}CHCH_2CH(OH)C_2H_5$ in 80% yield. The 250-MHz ^1H NMR spectrum of a sample isolated by GLC showed it to be the *E* isomer.

Reactions of (*E*)-2,4-Pentadienyltrimethylsilane with Ketones. The following general procedure was used. The apparatus was the same as in the aldehyde experiments described above. A solution of the ketone (6 mmol) in dry dichloromethane (6 mL) was cooled to −40 °C. Titanium tetrachloride (0.22 mL, 2 mmol) was added by syringe. The resulting solution was allowed to warm to room temperature, and the pentadienylsilane (4 mmol) then was added. The color of the mixture turned dark red; with time it became lighter. The mixture was stirred at room temperature for 2 h. Subsequent workup followed the procedure described above for the aldehyde reactions. The trap-to-trap distillation afforded almost pure product. Pure samples were obtained by GLC.

The products obtained when Me_2CO, Et_2CO, n-Pr_2CO, $MeC(O)CHMe_2$, and cyclohexanone were the ketones used have been prepared previously.[4] The spectra (IR and/or ^1H NMR) were identical with those reported. The 250-MHz ^1H NMR spectra of the products derived from acetone, diethyl ketone, and cyclohexanone were measured (in $CCl_4/CDCl_3$). J_{de} was measured as 15.0, 15.6, and 15.6 Hz, respectively (see proton designations for the pentadienyl group of the pivaldehyde product above and associated discussion). Thus all three ketone-derived products contained the (*E*)-2,4-pentadienyl group.

Reactions of (*E*)-2,4-Pentadienyltrimethylsilane with Crotonaldehyde and Mesityl Oxide. The procedure used in the case of the saturated aldehydes was applied in the case of crotonaldehyde. A single product, **3**, was obtained in 40% yield. A GLC sample had $n^{26}{}_D$ 1.4777. Its IR spectrum (liquid film) showed ν(C=C) at 1650, ν(C=O) at 1720, and the characteristic Me_3Si absorption at 1250 cm^{-1}. Two inseparable diastereoisomers were present, according to the 270-MHz proton NMR spectrum (in $CDCl_3$): δ 0.008 and 0.038 (2 s, 9 H, Me_3Si of the two diastereoisomers), 0.5 (m, 2 H, H_g), 1.02 (d, J = 7.15 Hz, 3 H, H_f), 1.8 (m, 1 H, H_e), 2.2 (br m, 3 H, H_d; never simplifies upon irradiation of any other signals), 2.5 (br m, 1 H, H_c; collapses to a d of t, J = 1.7, 8.3 Hz, upon irradiation of the m at 2.2), 5.6 (br s, 2 H, H_b), 9.69 (d, J = 3.2 Hz, H_a), 9.75 (d, J = 2.4 Hz, H_a). Anal. Calcd for $C_{12}H_{22}OSi$: C, 68.50; H, 10.54. Found: C, 68.79; H, 10.32.

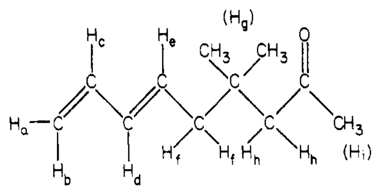


The two C*H*O resonances had an integrated ratio of 3:1, indicative of the presence of two diastereoisomers. The addition of DABCO did not change the ratio of the aldehyde resonances, which suggests that a thermodynamic mixture of isomers is present. Two much less intense signals at δ 9.47 and 9.49 may possibly be indicative of the presence of a minor amount of the other regioisomer.

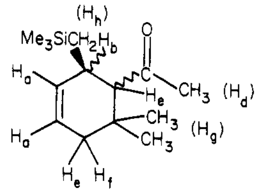
The reaction of (*E*)-2,4-pentadienyltrimethylsilane with mesityl oxide, $Me_2C{=}CHC(O)Me$, was carried out by using the general ketone reaction procedure. Two products were obtained.

(1) The Michael-type addition product: $n^{24}{}_D$ 1.4729; IR (liquid film) 3100 (m), 3040 (sh), 3020 (sh), 2970 (s), 2880 (s), 1719 (s), 1650 (m), 1600 (m), 1470 (m), 1450 (w), 1435 (w), 1420 (w), 1400 (w), 1385 (m), 1360 (s), 1210 (m), 1155 (m), 1010 (s), 955 (m), 900 (s), 840 (w) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.98 (s, 6 H, H_g), 2.09 (s, H_i), 2.1 (obscured by H_i, H_f, $H_i + H_f$ = 5 H), 2.29 (s, 2 H, H_h), 4.97 (d, J_{ac} = 10.26 Hz, 1 H, H_a), 5.09 (d, J_{bc} = 17.10 Hz, H_b), 5.67 (dt, J_{ef} = 7.82 Hz, 1 H, H_e), 6.02 (dd, J_{de} = 15.15 Hz, 1 H, H_d), 6.30 (ddd, J_{dc} = 10.7 Hz, 1 H, H_c). Anal. Calcd for

$C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.03; H, 10.85.



(2) The cyclized product: $n^{24}{}_D$ 1.4697; IR (liquid film) ν(C=O) 1720, ν(C=C) 1640, 1250 (Me_3Si) cm^{-1}; two inseparable diastereoisomers are present as evidenced by our GLC and NMR studies; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.010 and 0.021 (2s, 9 H, one for each diastereomer), 0.41 (m, 2 H, H_h), 0.90/0.96 (minor), 0.92/0.98 (major) (4s, 6 H, H_g; two pairs of singlets, one for each diastereomer), 1.70 (AB q, J = 18.9 Hz, 1 H, H_f), 1.96 (AB q, J = 18.9 Hz, 1 H, H_e), 2.18 (s, 3 H, H_d), 2.40 (d, J = 10.76 Hz, 1 H, H_c), 2.53 (br m, 1 H, H_b), 5.52 (br s, 2 H, H_a). Anal. Calcd for $C_{14}H_{26}OSi$: C, 70.51; H, 10.99. Found: C, 70.63; H, 10.83.



Reactions of (*E*)-2,4-Pentadienyltrimethylsilane with Acetals and Ketals. In a typical reaction, the acetal (6 mmol) was dissolved in 8 mL of dry dichloromethane, and the solution was cooled to −60 °C. Titanium tetrachloride (2 mmol) was added, and the mixture was stirred for 5 min and then cooled further to −78 °C. The pentadienylsilane (4 mmol) then was added, and the reaction mixture was stirred for 10 min at −78 °C. Subsequently, it was poured into 30 mL of saturated aqueous $NaHCO_3$. Extraction with diethyl ether (3 × 20 mL) followed. The dried (K_2CO_3) organic layer was concentrated at reduced pressure. The products were isolated by GLC (15% SE-30 on Chromosorb P).

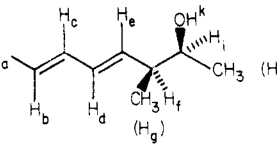
The pentadienylation of ketals was carried out by the same procedure except that longer reaction times at −78 °C were necessary (15 min in the case of $Me_2C(OMe)_2$; 30 min in the case of c-$C_6H_{10}(OEt)_2$). Also, the product yields were lower, and some nonvolatile, apparently polymeric by-products were formed.

The following ethers were prepared. (1) $Me_2CHCH_2CH(OEt)CH_2CH{=}CHCH{=}CH_2$, in 65% yield from $Me_2CHCH_2CH(OEt)_2$; $n^{20}{}_D$ 1.4610. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.92, H, 12.12. (2) $PhCH(OMe)CH_2CH{=}CHCH{=}CH_2$, in 79% yield from $PhCH(OMe)_2$; $n^{20}{}_D$ 1.5306. Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.80; H, 8.55. (3) $Me_2C(OMe)CH_2CH{=}CHCH{=}CH_2$, in 46% yield from $Me_2C(OMe)_2$; $n^{20}{}_D$ 1.4615. Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.89; H, 11.46. (4) c-$C(OEt)(CH_2CH{=}CHCHCH_2)CH_2CH_2CH_2CH_2CH_2$, in 40% yield from c-$C(OEt)_2CH_2CH_2CH_2CH_2CH_2$; $n^{20}{}_D$ 1.4897. Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.13; H, 11.38. The proton NMR spectra of all four ethers showed the presence of the (*E*)-2,4-pentadienyl group.

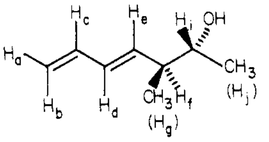
Reactions of (*Z,E*)-2,4-Hexadienyltrimethylsilane with Aldehydes. The reaction with acetaldehyde is typical.

In the usual apparatus a solution of 3.0 mmol of acetaldehyde was prepared in 25 mL of dry dichloromethane and cooled to −78 °C, and 2.0 mmol of $TiCl_4$ was added by syringe. The reaction mixture was stirred at −78 °C for 15 min; subsequently, 0.365 g, 2.4 mmol, of the hexadienylsilane in 10 mL of dichloromethane was added dropwise over a period of 10 min. The reaction mixture was stirred for 1 h at −78 °C and then, while at that temperature, treated with 10 mL of saturated aqueous $NaHCO_3$. The aqueous phase was separated and extracted with three portions of diethyl ether. The dried (K_2CO_3) organic layers were concentrated at reduced pressure, and the residue was trap-to-trap distilled into a liquid-nitrogen-cooled receiver. The distillate (0.219 g) was analyzed by GLC (6-ft Carbowax 20M on Chromosorb W, 70–150 °C program, 8 °C/min) showed it to contain (*E*)-3-methyl-4,6-heptadien-2-ol, $CH_2{=}CHCH{=}CHCHMeCH(OH)Me$ (0.181 g, 61% yield), as a mixture of diastereomers; $n^{20.5}{}_D$ 1.4820. Separation of the diastereomers was effected by GLC (6-ft Carbowax 20M, repeated injections on the analytical column); a 2:1 erythro/threo mixture was present.

^{1}H NMR (250 MHz, $CDCl_3$) (erythro isomer): δ 1.03 (d, J = 6.6 Hz, 3 H, H_g), 1.13 (d, J = 6.6 Hz, 3 H, H_j), 1.36 (d, J = 5.2 Hz, 1 H, OH), 2.26 (ddq, J_{ef} = 7.7, J_{fg} = 6.6, J_{fi} = 5.5 Hz, 1 H, H_f), 3.69 (ddq, J_{ij} = 6.6, J_{if} = 5.5, J_{ik} = 5.2 Hz, 1 H, H_i), 4.99 (dd, J_{ab} = 1.84, J_{ac} = 10.3 Hz, 1 H, H_a), 5.12 (dd, J_{ab} = 1.84, J_{bc} = 17.0, 1 H, H_b), 5.63 (dd, J_{de} = 15.1, J_{ef} = 7.7 Hz, 1 H, H_e), 6.08 (dd, J_{cd} = 10.3, J_{de} = 15.1 Hz, 1 H, H_d), 6.30 (ddd, J_{ac} = 10.3, J_{bc} = 17.0, J_{cd} = 10.3 Hz, 1 H, H_c).



^{1}H NMR (250 MHz, $CDCl_3$) (threo isomer): δ 1.01 (d, J = 6.8 Hz, 3 H, H_g), 1.16 (d, J = 6.2 Hz, 3 H, H_j), 2.13–2.16 (m, J_{ef} = 8.3, J_{fg} = 6.8, J_{fi} = 8.3 Hz, 1 H, H_f: determined by decoupling the CH_3 region and observing a "triplet (doublet of doublets)" for H_f, which gives $J_{if} = J_{ef}$), 3.54–3.60 (m, J_{ij} = 6.2, J_{if} = 8.3 Hz, 1 H, H_i), 5.01 (d, J_{ac} = 10.1 Hz, 1 H, H_a), 5.14 (d, J_{bc} = 17.6 Hz, 1 H, H_b), 5.49 (dd, J_{de} = 15.9, J_{ef} = 8.3 Hz, 1 H, H_e), 6.02 (dd, J_{cd} = 10.6, J_{de} = 15.9 Hz, 1 H, H_d), 6.13 (ddd, J_{ac} = 10.1, J_{bc} = 17.6, J_{cd} = 10.6 Hz, 1 H, H_c).

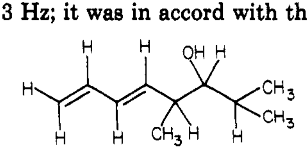


The observation that $^3J_{\text{threo}}$ (8.3 Hz) is greater than $^3J_{\text{erythro}}$ (5.5 Hz) is in line with literature reports on other threo/erythro systems.[17]

A satisfactory analysis of the alcohol could not be obtained, and, therefore, the trimethylsilyl ether was prepared on a 2.5-mmol scale by the hexamethyldisilazane procedure using a catalytic amount of trimethylchlorosilane. The product, $CH_2{=}CHCH{=}CHCH(CH_3)CH(OSiMe_3)CH_3$, was isolated by GLC. The proton NMR spectrum (250 MHz) showed two very close Me_3Si resonances at δ 0.087 and 0.073 in 1.8:1 integrated ratio, as well as overlapping peaks due to the diastereomeric methyl groups. Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18. Found: C, 66.35; H, 11.16. In the ^{1}H NMR spectrum of the diastereomeric mixture ^3J(erythro) and ^3J(threo) were observed to be 6.3 and 9.4 Hz.

A similar reaction of (*Z,E*)-2,4-hexadienyltrimethylsilane with propionaldehyde gave a 74:26 mixture of the diastereomers of (*E*)-4-methyl-5,7-octadien-3-ol, $CH_2{=}CHCH{=}CHCH(Me)CH(OH)CH_2CH_3$, in 51% yield; $n^{20.5}{}_D$ (isomer mixture) 1.4829. The ^{1}H NMR spectrum of this mixture of diastereomers was very similar to that of the acetaldehyde product in the pentadienyl region; ^3J(erythro) = 4.8 Hz. The trimethylsilyl ether was prepared as above, $CH_2{=}CHCH{=}CHCH(Me)CH(OSiMe_3)CH_2CH_3$. Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.86; H, 11.39. Found: C, 68.13; H, 11.48.

A reaction between (*Z,E*)-$CH_3CH{=}CHCH{=}CHCH_2SiMe_3$ and isobutyraldehyde at −78 °C in the presence of $TiCl_4$ in dichloromethane using the procedure above gave (*E*)-2,4-dimethyl-5,7-octadien-3-ol (84:16 erythro/threo ratio by GLC) in 37% yield. The ^{1}H NMR spectrum of the major isomer showed ^3J(erythro) = 5.3 Hz; it was in accord with the structure



Reactions of (*E*)-(4-Methyl-2,4-pentadienyl)trimethylsilane with Aldehydes. Reactions with propionaldehyde and pivaldehyde in dichloromethane in the presence of $TiCl_4$ at

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[17] E.g.: Mukaiyama, T.; Banno, K.; Narusaka, K. *J. Am. Chem. Soc.* **1974**, *96*, 7503 (β-keto alcohols). Yamamoto, Y.; Yatagai, H.; Maruyama, K. *Ibid.* **1981**, *103*, 3229 ($RCH(OH)CH(CH_3)CH{=}CHSiMe_3$).

temperatures ranging from −50 °C to room temperature using the general procedure which was successful in the case of (*E*)-2,4-pentadienyltrimethylsilane failed to give the desired products. After the usual workup and evaporation of the organic layer to remove solvent a viscous liquid residue invariably remained. No volatile products could be isolated from this material.

Acknowledgment. We are grateful to the U.S. Air Force Office of Scientific Research (NC)-AFSC for generous support of this work.

Registry No. **2**, 72952-73-9; **3**, 72952-63-7; **7**, 73400-23-4; **8**, 79210-77-8; **9**, 79210-79-0; **11** ($R = CH_3$), 82932-92-1; **11** ($R = CH_3$) Me_4Si, 82932-94-3; 11 ($R = CH_3CH_2$), 82932-96-5; 11 ($R = CH_3CH_2$) Me_4Si, 82932-98-7; **11** ($R = (CH_3)_2CH$), 82933-00-4; **12** ($R = CH_3$), 82932-93-2; **12** ($R = CH_3$) Me_4Si, 82932-95-4; **12** ($R = CH_3CH_2$), 82932-97-6; **12** ($R = CH_3CH_2$) Me_4Si, 82932-99-8; **12** ($R = (CH_3)_2CH$), 82933-01-5; (*E*)-$(CH_3)_2HSiCH_2CH{=}CHCH\Delta bdCH_2$, 82932-80-7; $CH_2{=}CHCH{=}CHCH_3$, 504-60-9; $CH_2{=}CHCH{=}CHCH_2K$, 51391-25-4; $CH_3CH{=}CHCH{=}CHCH_3$, 592-46-1; $CH_2{=}CHCH{=}CHCH(CH_3)K$, 82932-81-8; $CH_2{=}C(CH_3)CH_2CH{=}CH_2$, 763-30-4; C_2H_5CHO, 123-38-6; C_3H_7CHO, 123-72-8; $(CH_3)_2CHCHO$, 78-84-2; C_4H_9CHO, 110-62-3; $(CH_3)_3CCHO$, 630-19-3; $C_5H_{11}CHO$, 66-25-1; c-$C_6H_{11}CHO$, 2043-61-0; C_6H_5CHO, 100-52-7; $(cH_3)_2CO$, 67-64-1; $(C_2H_5)CO$, 96-22-0; $(C_3H_7)_2CO$, 123-19-3; $CH_3C(O)CH(CH_3)_2$, 563-80-4; $CH_3C(O)CH_2CH(CH_3)_2$, 108-10-1; $(CH_3)_2CHCH_2CH(OC_2H_5)_2$, 3842-03-3; $C_6H_5CH(OCH_3)_2$, 1125-88-8; $(CH_3)_2C(OCH_3)_2$, 77-76-9; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C_2H_5$, 72952-65-9; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C_3H_7$, 82932-82-9; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)CH(CH_3)_2$, 72952-66-0; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C_4H_9$, 82932-83-0; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C(CH_3)_3$, 72952-67-1; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C_5H_{11}$, 82932-84-1; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C_6H_{11}$-*c*, 72952-68-2; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OH)C_6H_5$, 72952-69-3; (*E*)-$CH_2{=}CHCH{=}CHCH_2C(OH)C(CH_3)_2$, 82932-85-2; (*E*)-$CH_2{=}CHCH{=}CHCH_2C(OH)(C_2H_5)_2$, 72952-70-6; (*E*)-$CH_2{=}CHCH{=}CHCH_2C(OH)(C_3H_7)_2$, 72952-71-7; (*E*)-$CH_2{=}CHCH{=}CHCH_2(OH)(CH_3)CH(CH_3)_2$, 82932-86-3; (*E*)-$CH_2{=}CHCH{=}CHCH_2C(OH)(CH_3)CH_2CH(CH_3)_2$, 82932-87-4; (*E*)-$CH_2{=}CH{=}CHCH_2C(OH)(CH_2)_5$, 72952-72-8; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OC_2H_5)CH_2iCH(CH_3)_2$, 82932-88-5; (*E*)-$CH_2{=}CHCH{=}CHCH_2CH(OCH_3)C_6H_5$, 82932-89-6; (*E*)-$CH_i{=}CHCH{=}CHCH_2C(OCH_3)(CH_3)_2$, 64586-00-1; (*E*)-$CH_2{=}CHCH{=}CHCH_2C(OC_2H_5)(CH_2)_5$, 82932-90-9; $Me_2C{=}CHC(O)Me$, 141-79-7; (*E*)-$CH_2{=}CHCH{=}CHCH_2C(CH_3)_2CH_2C(O)CH_3$, 72952-74-0; 1,4-pentadiene, 591-93-5; cyclohexanone, 108-94-1; cyclohexanone diethyl ketal, 1670-47-9; crotonaldehyde, 4170-30-3; acetaldehyde, 75-07-0; *cis*-3-(trimethylsilylmethyl)-4-acetyl-5,5-dimethylcyclohexene, 82932-91-0; *trans*-3-(trimethylsilylmethyl)-4-acetyl-5,5-dimethylcyclohexene, 82933-02-6.

Titanacyclobutanes: Substitution Pattern and Stability[†,‡]

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The relative stabilities of six alkyl-substituted titanacyclobutanes have been measured. For monosubstituted metallacycles, the substituent prefers the β-position. Addition of a second β substituent, such as CH_3, results in significant destabilization of the metallacycles. The relationship of ground-state stability to reactivity and the structural features influencing the stability are considered.

Introduction

Metallacyclobutanes have been implicated or demonstrated as intermediates in a number of catalytic and synthetic transformations.[1-3] Of major import in these reactions is the effect of substituents on the relative stabilities of the possible metallacyclic intermediates. For example, the selectivity observed in the olefin metathesis reaction has been attributed to differences in stability of the possible metallacyclic intermediates. We recently reported the synthesis of a series of metallacyclobutanes which undergo metathesis reactions. In this report we describe the effect of substituents on the relative stability of a series of titanacyclobutanes and examine the relationship between their relative stability and reactivity.

Experimental Section

Titanocene dichloride was purchased from Boulder Scientific and purified by Soxhlet extraction with dichloromethane. $AlMe_3$ was purchased from Alfa, or as a 2 M solution in toluene from Aldrich.[4] $AlMe_2Cl$ was purchased from Texas Alkyls. 4-(Dimethylamino)pyridine (DMAP) was purchased from Aldrich and recrystallized from hot toluene. 2,3-dimethyl-1-butene and 3,3-dimethyl-1-butene were purchased from Aldrich and stored over Linde 4-Å molecular seives. 2-Methyl-1-butene was purchased from ICN Pharmaceuticals and stored over molecular seives. 3-Methyl-1-butene was purchased from Phillips and stored over molecular seives. Isobutylene was purchased from Matheson and freeze-degassed twice prior to use. Tebbe reagent (**2**) prepared by an established procedure[5] was used for preparative purposes. For equilibrium measurements, **2** was prepared from $Cp_2TiMeCl$ and recrystallized from hexane.[6] $Cp_2\overline{TiCH_2CH(t\text{-}Bu)C}H_2$ (**1a**), $Cp_2\overline{TiCH_2CH(i\text{-}Pr)C}H_2$ (**1b**), and $Cp_2\overline{TiCH_2\underline{CHC}}\underline{H(C}H_2)_3$ (**4**)

[†] Dedicated to the memory of Rowland G. Pettit.

[‡] Contribution No. 6706.

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