fulvene **20** (360 mg) was obtained from diester **23** (0.6 g) in 81% yield. Recrystallization from cyclohexane furnished yellow crystals, mp 165 °C (dec) (reported mp 162 °C (dec)).[11] The spectral (UV-visible, NMR, mass) data for **20** were in agreement with those reported.[11]

2-(Formyl(1,3-dithiol-2-yl)methylene)-1,3-diselenole (24). A mixture of 1,3-dithiolium tetrafluoroborate[15] (100 mg) and aldehyde **13** (100 mg) in THF (10 mL) was stirred at room temperature for 1 h. The solvent was evaporated and the residue was subjected to flash chromatography (SiO_2, benzene) to give product **24** (112 mg, 77%), which was crystallized from methanol to give yellow needles of **24**, mp 138 °C; IR spectrum, 1600 cm^{-1} (>CO); ^1H NMR spectrum, δ 9.55 (s, 1 H), 7.99 (AB q, J = 9 Hz, 2 H), 6.54 (s, 1 H), 6.14 (s, 2 H); mass spectrum, m/e (relative intensity) 342 (98.8), 340 (100), 313 (37.5), 182 (80.6), 103 (76.9); UV-visible spectrum, $\lambda_{max}^{CH_2Cl_2}$ 227.1 nm (ϵ 16 768), 251.8 (18 431), 395.6 (30 034). Anal. Calcd for $C_8H_6OS_2Se_2$: C, 28.10; H, 1.77. Found: C, 28.20; H, 1.79.

Reaction of 2-Benzylidene-4-phenyl-1,3-diselenole (5) with Benzoyl Chloride. A solution of **5** (364 mg) in CH_2Cl_2 (5 mL) was treated with benzoyl chloride (0.12 mL). Shiny yellow plates separated, which were filtered, washed, and dried to give the trans isomer of **5** (330 mg), mp 228 °C, identical (IR, MS, mp) with an authentic sample prepared according to ref 3.

The above reaction was also carried out in the presence of pyridine as solvent (3 mL). The reaction mixture was heated at 100 °C for 2 h. Workup led to the isolation of starting material (200 mg).

Attempted Coupling of Aldehyde 13 with $TiCl_4$-LAH. To a suspension of LAH (4 mg) in dry THF (5 mL) was added via syringe a solution of $TiCl_4$ (0.5 mL) in THF (3 mL). An exothermic reaction ensued, leading to a yellow solution. To this solution was added a mixture of aldehyde **13** (200 mg) and triethylamine (0.12 mL) in dry THF (6 mL). The mixture was refluxed overnight. The cooled reaction mixture was diluted with 20% aqueous K_2CO_3 and extracted with benzene. Evaporation of benzene led to the recovery of starting material.

Attempted Desulfurization of Thioaldehyde 15.[16] A solution of **15** (0.95) and hexabutyldistannane (2.2 mL) in benzene (1.0 L) was photolyzed for 14 h using a medium-pressure lamp. The solvent was evaporated. The residue was extracted with hexane. The residue from the hexane-soluble fraction (2.6 g) was malodorous, and the TLC (SiO_2, $CHCl_3$-hexane (1:1)) was complex. Chromatographic resolution led to the partial purification of the product(s). Two components were identified by mass spectrometry as recovered hexabutyldistannane (0.9 g) and hexabutylditin selenide ($(Bu_3Sn)_2Se$ (0.6 g)).

Acknowledgment. This work was supported by a grant from the National Science Foundation (Grant NSF-86-07458).

(14) Lakshmikantham, M. V.; Cava, M. P. *J. Org. Chem.* **1976**, *41*, 882.
(15) Wudl, F.; Kaplan, M. L. *J. Org. Chem.* **1974**, *39*, 3608.
(16) This reaction was based on the reported desulfurization of 1,3-dithiole-2-thione by: Ueno, Y.; Nakayana, A.; Okanava, M. *J. Am. Chem. Soc.* **1976**, *98*, 7440.

Anion-Catalyzed Reactions of Silyl Ester Polyenolates with Electrophiles†

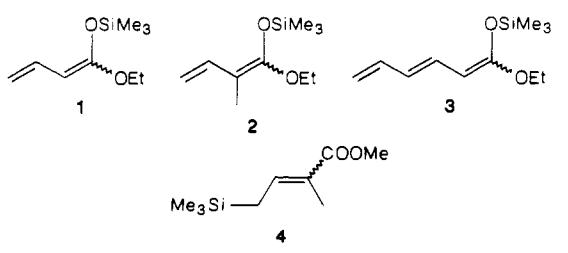
Walter R. Hertler,* Gade S. Reddy, and Dotsevi Y. Sogah

Central Research and Development Department, E. I. du Pont de Nemours and Co., Inc., Experimental Station, Wilmington, Delaware 19898

Received August 27, 1987

The stereochemical assignments for the trimethylsilyl ester polyenolates **1**, **2**, and **3** have been made. Unlike simple silyl ketene acetals, **1**, **2**, and **3** are obtained predominantly as the thermodynamic *Z* isomers. Bifluoride-catalyzed equilibration studies showed the equilibrium compositions of **1**, **2**, and **3** to be 89% *Z*, 67% *Z*, and 95% 1-*Z*,3-*E*, respectively. The regiochemistry of the bifluoride-catalyzed Reformatsky-type reaction of benzaldehyde with **1**, **2**, and **4** was determined. Regiochemical control of the condensation of **1** with benzaldehyde by reaction temperature was demonstrated, with 95% α reaction at −95 °C and 99% γ-reaction at +34 °C. Mechanism studies are consistent with a dissociative process in which a dienolate reacts with benzaldehyde at the α position to give the kinetic-controlled product, and as the reaction temperature increases, increasing amounts of the thermodynamic γ product are formed. A nondissociative cyclic process leading to α product may occur at low temperatures. The naked ester dienolate prepared by reaction of **1** with TASF and removal of the resulting fluorotrimethylsilane was alkylated by benzyl bromide exclusively at the α position at −100 °C. The bifluoride-catalyzed reverse reaction of **1** with benzaldehyde is much slower than the processes that determine the regiochemistry in the forward reaction.

The importance of development of synthetic methodologies for the formation of carbon–carbon double bonds has stimulated interest by several research groups in studies of carbon–carbon bond-forming reactions of carbon electrophiles with silyl ester polyenolates such as **1** and **2**, lithium ester polyenolates, and dilithium acid polyenolates.[1-13] In general, the regiochemistry of the reactions



† Contribution no. 4373.

(1) Fleming, I.; Goldhill, J.; Paterson, I. *Tetrahedron Lett.* **1979**, *20*, 3209.
(2) (a) Fleming, I.; Goldhill, J.; Paterson, I. *Tetrahedron Lett.* **1979**, *20*, 3205. (b) Fleming, I.; Iqbal, J. *Tetrahedron Lett.* **1983**, *24*, 2913.
(3) Paterson, I.; Price, L. G. *Tetrahedron Lett.* **1981**, *22*, 2833.
(4) Oida, T.; Tanimoto, S.; Ikehira, H.; Okano, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 645.
(5) (a) Bellassoued, M.; Gaudemar, M. *J. Organomet. Chem.* **1984**, *263*, C21. (b) Bellassoued, M.; Ennigrou, R.; Gaudemar, M. *J. Organomet. Chem.* **1988**, *338*, 149.
(6) Fleming, I.; Iqbal, J.; Krebs, E.-P. *Tetrahedron* **1983**, *39*, 841.
(7) Lam, C. N.; Mellor, J. M.; Rawlins, M. F.; Stibbard, J. H. A. *Tetrahedron Lett.* **1978**, *19*, 4103.
(8) Hermann, J. L.; Kieczykowski, G. R.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, *14*, 2433.
(9) Katzenellenbogen, J. A.; Drumrine, A. L. *J. Am. Chem.* Soc. **1974**, *96*, 5662.

0022-3263/88/1953-3532$01.50/0

was found to be highly variable, depending on the nature of the electrophile, the metal or silicon enolate, and the reaction temperature.

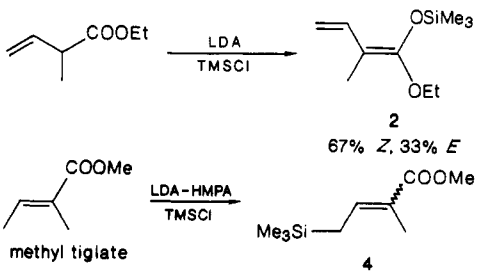
Because of the quantitative yields and well-defined regio- and stereochemistry reported for group-transfer polymerization,[14a,b] we chose to approach the problem of regio- and stereoselectivity in reactions of silylpolyenolates with electrophiles by using the same anion catalysts.[14c] We studied the anion-catalyzed Reformatsky-type reactions of the known silyl ester dienolates **1** and **2** and the *C*-silyl analogue of **2** (**4**) with benzaldehyde. This paper details our study of the remarkable effect of the reaction temperature on regiochemistry and the mechanistic implications of the temperature dependence. By assigning, for the first time, the stereochemistry of **1**, **2**, and **3**, we have found that, unlike simple silyl ketene acetals, these silyl ester polyenolates are largely the thermodynamic *Z* isomers whether prepared under normally equilibrating or nonequilibrating conditions.

Synthesis and Stereochemistry

1-Ethoxy-1-(trimethylsiloxy)butadiene (**1**) was prepared from ethyl crotonate (lithium diisopropylamide–hexamethylphosphoramide–chlorotrimethylsilane (LDA–HMPA–TMSCl))[2,8] as well as from ethyl 3-butenoate (LDA–TMSCl).[5,15] Contrary to expectations, both preparative methods produced **1** with similar stereochemistry, predominantly as a single isomer. Since there was no stereochemical assignment for **1** in the literature, we made use of NOE in the ^{1}H NMR spectrum, which showed the major isomer to be *Z* (see Experimental Section). The methyl analogue of **1**, 1-methoxy-1-(trimethylsiloxy)-1,3-butadiene, was recently prepared by Brandstadter, Ojima, and Hirai[16] as a 1:1 *E*:*Z* mixture. Partial fractionation of **1** by distillation gave fractions ranging from 75% *Z* to 90% *Z*. About 80% of the total product was *Z*. For our studies of the Reformatsky-type reactions of **1**, we used (90% *Z*)-**1**.

Equilibration studies carried out on a sample of **1** having the composition 75% *Z*,25% *E* using HgI_2 catalyst[17] gave 89% *Z*,11% *E* as the equilibrium composition, while a similar treatment of a 90% *Z*,10% *E* mixture produced virtually no change. This shows that the 90% *Z*,10% *E* composition obtained by distillation is the equilibrium composition. Treatment of (75% *Z*,25% *E*)-**1** in THF-d_8 solution with 1 mol % of tris(*N*-piperidinyl)sulfonium bifluoride ($TPSHF_2$)[18] gave instantaneous formation of a yellow color (as we have always observed upon treatment of **1** with an anion catalyst) and led to equilibration to the same (within experimental error) isomeric mixture of **1** (91% *Z*, 9% *E*) within 44 min (the time of the initial ^{1}H NMR observation). In the absence of catalyst, however, the isomeric composition of a nonequilibrium sample of **1** was entirely unchanged after storage for 2.5 years. The bifluoride-catalyzed equilibration of (*E*)- and (*Z*)-**1** appears to be much faster than the bifluoride-catalyzed *E*/*Z* equilibration of the silyl ketene acetal, 1-methoxy-1-(trimethylsiloxy)-1-propene.[14b] In contrast to simple silyl ketene acetals, which are normally obtained as the predominantly *E* (kinetic control) isomer under nonequilibrating conditions,[19] the silyl dienolate **1**, even in the absence of HMPA, is obtained predominantly as the *Z* isomer. The stereochemical results are consistent with either a more rapid formation of the *Z* isomer or a more facile *E*/*Z* equilibration in extended conjugated unsaturated systems than in the unconjugated ones. Whether the anion-catalyzed *E*/*Z* isomerization of **1** proceeds via the **1**–catalyst complex without dissociation or via the free dienolate is not clear. However, the rapid anion-catalyzed equilibration of **1** has implications for the stereoselectivity of anion-catalyzed reactions of silyl ester polyenolates.

Scheme I



1-Ethoxy-1-(trimethylsiloxy)-2-methylbutadiene (**2**), prepared from ethyl 2-methyl-3-butenoate (LDA–TMSCl),[20] was obtained as a 2:1 mixture of *Z* and *E* isomers (Scheme I). The stereochemistry was determined from the ^{1}H NMR spectrum using NOE. Because there was no fractionation of the geometric isomers in distillation of **2**, we did not have available a sample of **2** with an isomeric composition other than 2:1 *Z*:*E* to use for equilibration studies. Treatment of the available isomeric mixture of **2** with 1% $TPSHF_2$ in THF-d_8 led to no change in the ratio of *Z* and *E* isomers. This provides evidence that the equilibrium composition of **2** is 2:1 *Z*:*E*, and the synthesis of **2** provides the equilibrated product. Brandstadter, Ojima, and Hirai[16] have reported the stereochemistry of the methyl analogue of **2**, 1-methoxy-1-(trimethylsiloxy)-2-methyl-1,3-butadiene, to be 1:1 *E*:*Z*.

Attempts to prepare the methyl analogue of **2** using the LDA–HMPA–TMSCl procedure gave only the *C*-silyl ester **4**. Bellassoued et al.[5b] recently reported a similar formation of the trimethylsilyl ester of (*E*)-4-(trimethylsilyl)-2-butenoic acid from the reaction of either crotonic acid or 3-butenoic acid with 2 equiv of a lithium amide followed by TMSCl. The ^{1}H NMR spectrum of **4** is consistent with a single isomer, which we presume to be the *E* isomer.

1-Ethoxy-1-(trimethylsiloxy)-1,3,5-hexatriene (**3**) was synthesized from ethyl 3,5-hexadienoate (LDA–TMSCl). The stereochemical assignment (95% *Z*,*E*; 5% *E*,*E*) was based upon the ^{1}H NMR spectrum, which was analyzed with reference to the spectra of the *E* and *Z* isomers of **1**. Only a single isomeric composition of **3** was obtained, as

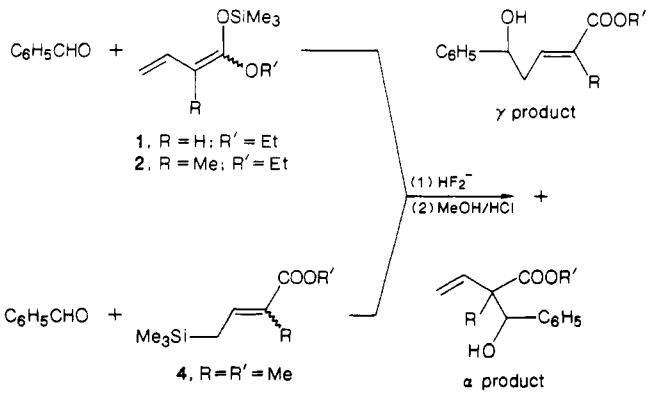
(10) Casinos, I.; Mestres, R. *J. Chem. Soc., Perkin Trans.* 1, **1978**, 1651.
(11) Johnson, P. R.; White, J. D. *J. Org.* Chem. **1984**, *49*, 4424 and references cited therein.
(12) Ballester, P.; Garcia-Raso, A.; Gomez-Solivellas, A.; Mestres, R. *Tetrahedron Lett.* **1985**, *26*, 2485.
(13) Ballester, P.; Costa, A.; Garcia-Raso, A.; Gomez-Solivellas, A.; Mestres, R. *Tetrahedron Lett.* **1985**, *26*, 3625.
(14) (a) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706. (b) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473. (c) Dicker, I. B.; Cohen, G. M.; Farnham, W. B.; Hertler, W. R.; Laganis, E. D.; Sogah, D. Y. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1987**, *28*(1), 106.
(15) Bellassoued, M.; Dardoize, F.; Frangin, Y.; Gaudemar, M. *J. Organomet. Chem.* **1981**, *219*, C1.
(16) Brandstadter, S. M.; Ojima, I.; Hirai, K. *Tetrahedran Lett.* **1987**, *28*, 613.
(17) The use of HgI_2 to catalyze *E*–*Z* isomerizations of silyl ketene acetals has been reported by: Dicker, I. B. *Abstracts of Papers*, 189th National Meeting of the American Chemical Society, Miami, FL; American Chemical Society: Washington, DC, 1985; ORGN 238.
(18) (a) Middleton, W. J. U.S. Patent 3 940 402, 1976. (b) Brittain, W. J. *J. Am. Chem. Soc.*, in press.
(19) See, for example: (a) Corey, E. J.; Gross, A. W. *Tetrahedron Lett.* **1984**, *25*, 495. (b) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868. (c) RajanBabu, T. V. *J. Org. Chem.* **1984**, *49*, 2083.
(20) Savard, J.; Brassard, P. *Tetrahedron* **1984**, *40*, 3455.

Table I. Products of Bifluoride-Catalyzed Reaction of Benzaldehyde with 1, 2, and 4

entry	silyl compd	temp, °C	γ-product, %	α-product, %	% yield[a]
1	1 (90% Z)	34	99	1	94
2	1 (90% Z)	0	96	4	95
3	1 (90% Z)	-28	74	26	91
4	1 (90% Z)	-50	32	68	96
5	1 (90% Z)	-50[b]	32	68	96
6	1 (90% Z)	-95	3	97	84
7	1 (90% Z)[a,c]	-95	5	95	78
8	1 (90% Z)[a,d]	-30	25	75	94
9	1 (75% Z)	15	98	2	76
10	1 (75% Z)	0	95	5	76
11	1 (75% Z)	-28	65	35	83
12	1 (75% Z)	-50	28	72	76
13	2 (67% Z)[a]	32	100	0	79
14	2 (67% Z)[a]	-23.5	100	0	88
15	2 (67% Z)[a]	-62	81	19	78
16	2 (67% Z)[a]	-63	77	23	88
17	2 (67% Z)[a]	-73	56	44	75
18	2 (67% Z)[a]	-73[b]	49	51	88
19	4	28.5	99.3	0.6	89
20	4	-78	64	36	tr
21	4[d]	-30	76	24	100

[a] Product analysis by 360-MHz ^{1}H. [b] Temperature allowed to warm to 25 °C before quenching with methanolic HCl. [c] 0.3% tetrabutylammonium acetate used instead of 0.3% $TASHF_2$. [d] *p*-Nitrobenzaldehyde used instead of benzaldehyde.

Scheme II



fractionation of isomers did not occur during distillation. Since treatment of **3** with 1% $TPSHF_2$ in THF-d_8 left the 95% *Z,E*:5% *E,E* composition unchanged (although loss of 30% of **3** by decomposition was observed), this appears to be the equilibrium composition. A similar synthesis of the methyl analogue of **3**, 1-methoxy-1-(trimethylsiloxy)-1,3,5-hexatriene, of unknown stereochemistry was recently reported.[21]

Reactions with Electrophiles

The reaction of **1**, **2**, and **4** with benzaldehyde was carried out in THF in the presence of 0.3 mol % of tris(dimethylamino)sulfonium bifluoride ($TASHF_2$). The $TASHF_2$ was introduced as a 1.0 M solution in acetonitrile due to the low solubility of $TASHF_2$ in THF. The addition of **1** was slow enough that isothermal conditions (±1 °C) were maintained, and the products were identified by GC and/or ^{1}H NMR after quenching with methanolic acid (Scheme II). The results are summarized in Table I. It is apparent from entries 1–7 that there is a strong dependence of the regiochemistry of the Reformatsky-type reaction of **1** (90% *Z*) with benzaldehyde on the reaction temperature, and, in fact, nearly regiospecific condensations are obtained at the extremes of temperature studied, 99% γ product at +34 °C (entry 1) and 97% α product at -95 °C (entry 6). The preference for α reaction at low temperature and γ reaction at higher temperatures is similar to the behavior of dilithium acid dienolates with carbonyl compounds studied by Casinos and Mestres.[10] These authors found that the α adducts formed at low temperature isomerized to γ adducts on heating. In contrast to these results, however, when **1** was allowed to react with benzaldehyde at -50 °C and then held at 25 °C for 1 h before quenching, the α:γ ratio was the same as when the reaction was quenched at -50 °C (Table I, entries 4 and 5). If the regiochemistry at a given temperature is the result of the relative rates of reaction at the α and γ positions at that temperature, the differences in activation parameters, $\Delta\Delta H^{\ddagger}$, $\Delta\Delta S^{\ddagger}$, and $\Delta\Delta G^{\ddagger}$, for γ- and α-reaction pathways can be calculated from the plot of ln (C_γ/C_α) versus reciprocal temperature (Arrhenius), where C_γ and C_α are the concentrations of γ and α product. Figure 1 shows such a plot for entries 1–4 and 6 of Table I (with error limits equal to ±3 times the standard deviation of the regression). The values calculated for the difference between γ and α reaction are $\Delta\Delta H^{\ddagger} = 7 \pm 2$ kcal·mol^{-1}, $\Delta\Delta S^{\ddagger} = 31 \pm 8.7$ eu, and $\Delta\Delta G^{\ddagger} = -1.7 \pm 0.5$ kcal·mol^{-1} (at 273 K). It is apparent that enthalpy favors reaction at the α position, while entropy favors reaction at the γ position. Consistent with enthalpy-controlled α reaction, we found that when a more reactive aldehyde, *p*-nitrobenzaldehyde, was used, the resulting product was richer in the α isomer (75% α, 25% γ, entry 8) than was obtained with benzaldehyde (26% α, 74% γ, entry 3).

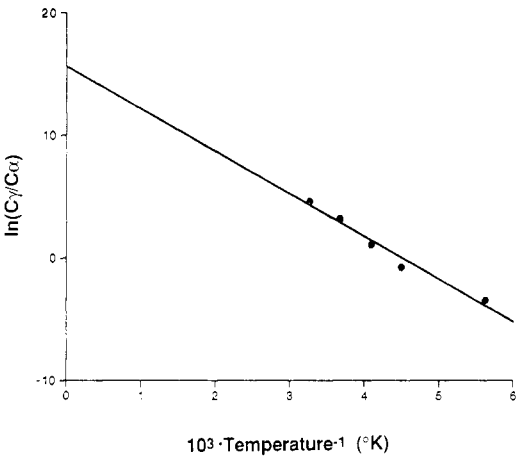


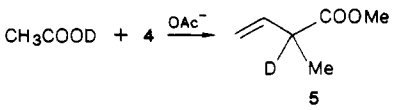
Figure 1. Arrhenius plot for the reaction of **1** with benzaldehyde at the α- and γ-positions.

When tetrabutylammonium acetate was used as catalyst instead of $TASHF_2$ at -95 °C, the resulting product mix was 95% α-, 5% γ-hydroxy ester (Table I, entry 7), essentially the same ratio obtained with bifluoride (97% α, 3% γ, entry 6). The isomeric content of **1** does not have any observable effect on the regioselectivity. Thus, a 75% *Z*,25% *E* mixture gave almost the same regioselectivity as the 90% *Z*,10% *E* mixture (entries 9–12). This suggests that initial silyl dienolate geometry is not an important determinant of regioselectivity and is consistent with the observed *E*/*Z* mobility in the presence of an anion.

In contrast to the temperature-controlled regiochemistry, there is essentially no diastereoselectivity for erythro or threo, since approximately equal amounts of erythro and threo α adducts were observed in all experiments. This lack of diastereoselectivity is consistent with the low diastereoselectivity observed in the bifluoride-catalyzed reactions of aldehydes with silyl ketene acetals[22] and the

(21) Ohno, M.; Mori, K.; Eguchi, S. *Tetrahedron Lett.* **1986**, *27*, 3381.

Scheme III



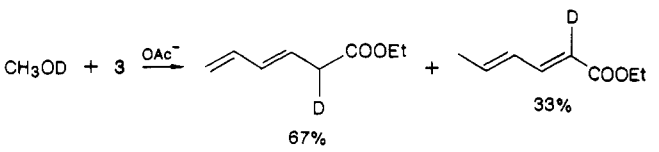
5

absence of diastereoselectivity recently reported in the fluoride-catalyzed reaction of benzaldehyde with 1,1-bis-(trimethylsiloxy)-1,3-butadiene.[5b] Regarding double-bond stereochemistry, only *E*, but no *Z*, isomers of the γ products were detected at all temperatures investigated.

Whatever the mechanism, to the extent that steric factors play a role, a substituent at the α position would be expected to increase the energy of the transition state leading to α substitution. To investigate the effect of substitution on regiochemistry, the reaction of **2** (67% *Z*) with benzaldehyde was studied at several different reaction temperatures (Table I, entries 13–18), and the products were analyzed by NMR rather than by GC. The effects of temperature on the regiochemistry of this reaction are similar to those described for **1** in that, at higher temperatures, there is a pronounced regioselectivity for γ-adduct formation, with increasing α-adduct formation as temperature is lowered. However, as expected from steric considerations, there is a greater tendency for reaction at the γ position in **2** than in **1** at all temperatures. At −23.5 °C **2** gives 100% γ adduct, while at −28 °C **1** gives 74% γ product (entries 14 and 3). At −73 °C, the lowest temperature studied with **2**, almost equal amounts of γ and α products are formed (entry 17). The greater tendency in **2** than in **1** for reaction at the γ position is reflected in the estimated $\Delta\Delta G^{\ddagger}_{273}$ of −3.6 kcal·mol^{-1} for **2** and −1.7 kcal·mol^{-1} for **1**. When the reaction of **2** with benzaldehyde at −73 °C is allowed to warm to 25 °C before quenching (Table I, entry 18), the change in product mixture is insignificant (56% γ/44% α to 49% γ/51% α). Although there is no pronounced diastereoselectivity in the reaction of **2** with benzaldehyde, slightly more threo (57%) than erythro (43%) ethyl 2-methyl-2-(α-hydroxybenzyl)-3-butenoate is obtained from the reaction at −63 °C.

The allylic silane **4** is of particular interest since, except for the presence of an *O*-methyl group instead of an *O*-ethyl group, it is a tautomer of the silyl ester dienolate, **2**. As is characteristic of *O*-silyl and *C*-silyl isomeric compounds, the *C*-silyl **4** is far less reactive than **2**.[14b] Thus, the tetrabutylammonium acetate catalyzed reaction of **4** with acetic acid-*d* in THF solution was slow and gave only 7% conversion to methyl 2-deuterio-2-methyl-3-butenoate (**5**), even after 2 days at room temperature (Scheme III). The bifluoride-catalyzed reaction of **4** with benzaldehyde at −78 °C gave only a trace of product, undetectable by NMR, but found by GC to be 64% γ adduct and 36% α adduct (Table I, entry 20). At 28.5 °C γ adduct was formed almost exclusively (entry 19). The resulting methyl 2-methyl-5-phenyl-5-(trimethylsiloxy)-2-pentenoate was isolated, characterized, and then hydrolyzed to methyl 2-methyl-5 phenyl-5-hydroxy-2-pentenoate. Thus, **4** shows a preference for reaction at the γ position similar to **2**. Bellassoued et al. reported a modest preference for γ reaction of trimethylsilyl 4-(trimethylsilyl)-2-butenoate with benzaldehyde catalyzed by tetrabutylammonium fluoride at 20 °C.[5b] Snieckus and co-workers[23] found that *N,N*-dimethyl-3-methyl-4-(trimethylsilyl)-2-butenamide gave only γ addition with benzaldehyde with fluoride catalyst at 20 °C, similar to our finding with **4**. Under kinetic conditions (stoichiometric fluoride, −45 °C, 2 min) they found 92% α reaction with essentially no diastereoselectivity. The bifluoride-catalyzed reaction of **4** with *p*-nitrobenzaldehyde at −30 °C gave a quantitative yield of 76% γ adduct and 24% α adduct (entry 21), but in this case the α adduct consisted of a 2:1 ratio of threo:erythro isomers. The γ-isomer crystallized and was fully characterized.

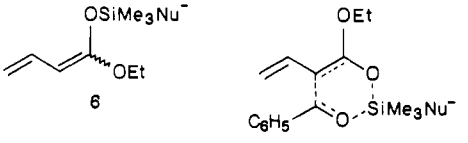
Scheme IV



Anion-catalyzed protonation of the silyl ester trienolate **3** was examined by using tetrabutylammonium acetate and methanol-*d*. The major product (67%) was ethyl 2-deuterio-3,5-hexadienoate, and the minor product (33%) was ethyl 2-deuteriosorbate (Scheme IV). ^{1}H NMR studies showed that both products were approximately 50% deuteriated in the 2 positions, and little, if any, deuterium was detected in the ω positions. Since only 2-deuterio products were observed, it is apparent that α protonation of the trienolate predominated. Perhaps the ethyl sorbate resulted from subsequent isomerization. Preferential α protonation of the silyl trienolate is consistent with the reported α protonation and alkylation of the lithium trienolate derived from sorbic acid or its methyl ester.[24-26]

Mechanism Studies

A nondissociative mechanism has been established by Sogah and Farnham[27] for the bifluoride-catalyzed Michael addition of methyl methacrylate to silyl ketene acetal ended polymers. An analogous nondissociative process must be considered for the reaction of benzaldehyde with silyl ester dienolates. In a nondissociative process **6**, the complex between **1** and the anion catalyst, reacts with



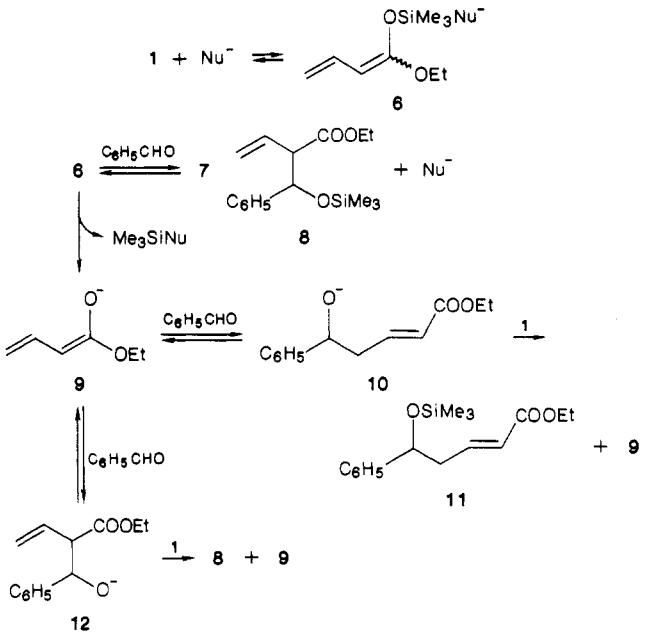
6 7

benzaldehyde without prior dissociation to the dienolate. Reaction of benzaldehyde with **6** at the α position can proceed via a cyclic transition state **7**, leading directly to α-siloxybenzyl ester **8**. The anion-catalyzed *E*/*Z* isomerization of **1**, which we have demonstrated, can account for the lack of diastereoselectivity in the α product. However, the reaction of benzaldehyde with **6** at the γ position cannot involve such a cyclic transition state, leading to (*E*)-γ-siloxybenzyl ester **11**. It appears that dissociation of the silicon is inevitable prior to formation of **11**.

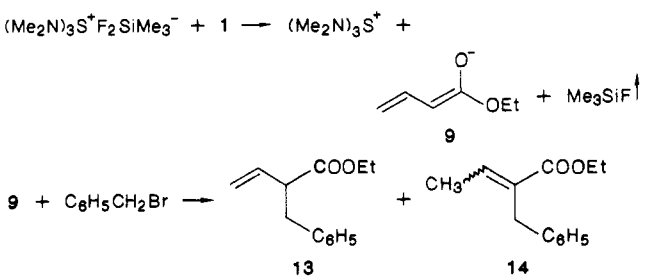
Although a nondissociative mechanism can provide a pathway for α product, a mechanism that can provide pathways for formation of both α and γ product is the dissociation of **6** to the naked dienolate **9**, which then reacts with the benzaldehyde at the α or γ position as outlined

(22) Sogah, D. Y. (a) U.S. Patent 4 448 980, 1984. (b) Unpublished results.
(23) Majewski, M.; Green, J. R.; Snieckus, V. *Tetrahedron Lett.* **1986**, *27*, 535.
(24) Yoshida, K.; Grieco, P. A. *J. Org. Chem.* **1984**, *49*, 5527.
(25) Bremmer, M. L.; Weinraub, S. M. *Tetrahedron Lett.* **1983**, *24*, 261.
(26) Snider, B. B.; Phillips, G. B.; Cordova, R. *J. Org. Chem.* **1983**, *48*, 3003.
(27) Sogah, D. Y.; Farnham, W. B. *Organosilicon and Bioorganosilicon Chemistry: Structures, Bonding, Reactivity, and Synthetic Application*; H. Sakurai, Ed.; Wiley: New York, 1985; Chapter 20.

Scheme V



Scheme VI



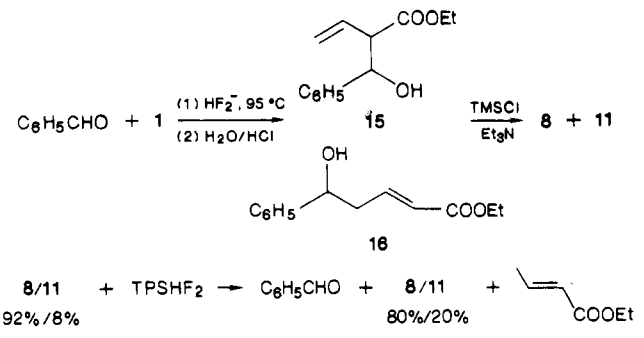
in Scheme V. The experimental observations can be accommodated by the proposed mechanism (Scheme V) in which, at low temperature, the nondissociative pathway via **7** may predominate. At higher temperatures the dissociative process via **9** becomes increasingly important. To the extent that the dissociative process occurs at low temperatures, the reaction of **9** with benzaldehyde at the α position to form the alkoxide **12** is kinetically faster than reaction at the γ position to form the alkoxide **10**. At low temperatures the kinetic product predominates, while at higher temperatures more of the thermodynamic γ product is formed. The alkoxides **10** and **12** undergo silylation by **1** to form **11** and **8**, respectively, along with more **9** in a process that is essentially irreversible on the time scale of the other processes. Silylation of the alkoxides **10** and **12** is certain to be by reaction with **1** rather than Me_3SiNu because of the expected[19c] much greater silylating reactivity of **1** and its much higher concentration. Thus, there is continual regeneration of **9**, and its concentration is always very low (never higher than the catalyst concentration, 0.3%). The observed low diastereoselectivity is consistent with configurational lability of **9**. The dissociative mechanism can satisfactorily account for the temperature-dependent regioselectivity without invoking a nondissociative mechanism at low temperatures. A detailed kinetic study would be required in order to asess the relative importance of dissociative and nondissociative processes, and such a study is beyond the scope of this paper. Considering the complex equilibria involved in the proposed mechanism, it would be inappropriate to attempt to use the calculated activation parameter differences as probes for mechanistic pathways.

The proposed mechanism (Scheme V) assumes that **9** will react preferentially at the α position at low temperature. Although it seems to be generally assumed[5b,8] that ester dienolates are most reactive toward electrophiles at the α position, particularly in irreversible reactions such as alkylation, most evidence for preferential α reaction is based on studies of lithium ester dienolates,[8] where coordination of the metal with the anion occurs. Such systems may not be valid models for naked dienolates. In the study of Snieckus and co-workers,[23] a stoichiometric reaction of tetrabutylammonium fluoride with *N,N*-dimethyl-3-methyl-4-(trimethylsilyl)-2-butenamide and benzaldehyde at −45 °C led to 92% α and 8% γ product. However, it is not clear in this case to what extent a naked dienolate was present since the silicon was still present in the reaction mixture and available for resilation of any dienolate. We applied the technique of Noyori[28] to the preparation of the TAS ester dienolate, TAS 1-ethoxy-1,3-butadien-1-olate (**9**). Following the reaction of stoichiometric quantities of TASF and **1** in THF at −100 °C, diethyl ether was added and codistilled with the resulting fluorotrimethylsilane at −41 °C under reduced pressure. In a cold trap 70% of the theoretical fluorotrimethylsilane was recovered. Rapid addition of benzyl bromide to the TAS dienolate **9** at −100 °C led to formation of ethyl 2-benzyl-3-butenoate (**13**) and ethyl 2-benzyl-2-butenoate (**14**) in a ratio (determined by GC) of 9:1 (Scheme VI). The minor product **14** presumably arises from double-bond isomerization of **13** under the strongly basic reaction conditions. The structure of **14** was confirmed by NMR decoupling experiments (see Experimental Section). No ethyl 5-phenyl-2-butenoate resulting from γ alkylation was detected. Thus, in an alkylation reaction the naked dienolate shows a very strong preference for reaction at the α position at −100 °C, consistent with the proposed mechanism. In a similar experiment using benzaldehyde instead of benzyl bromide, the principal product, as determined from GC/MS, resulted from 2:1 condensation of benzaldehyde with the TAS dienolate and was not identified. Thus, we were unable to determine a useful α:γ reactivity in the Reformatsky-type reaction of a naked dienolate, since the normal products were minor components.

It is assumed in the proposed mechanism (Scheme V) that, under the reaction conditions, the α and γ products **8** and **11** cannot interconvert either by direct isomerization or by reversal to form **9**. The observation that the regiochemical composition of the product formed at low temperature was retained after warming to room temperature (Table I, entries 4 and 5) suggests that reversibility is not facile for the silylated product. To address this question and to determine the limits of product stability under the reaction conditions, the $TPSHF_2$-catalyzed reaction of **1** with benzaldehyde was carried out preparatively at about −95 °C with a low-temperature acid quench to give a mixture of hydroxy esters of which 92% was the α product **15** and 8% was the γ product **16** (Scheme VII). The α product consisted of about equal amounts of erythro and threo diastereomers. The isomeric mixture was silylated with chlorotrimethylsilane and triethylamine to give the trimethylsiloxy esters **8** (92%) and **11** (8%). Observation by ^1H NMR of a solution in THF-d_8 of 92% **8** and 8% **11** in the presence of 0.3% $TPSHF_2$ showed that after 45 min., 5.5% of benzaldehyde had formed, and the starting material consisted of 20% **11** and 80% **8**. This composition was unchanged after an additional 18 h. A similar ex-

(28) Noyori, R.; Nishida, I.; Sakataa, J. *J. Am. Chem. Soc.* **1983**, *105*, 1598.

Scheme VII



periment with 0.9 mol % of $TPSHF_2$ catalyst showed formation of 30% benzaldehyde, and the remaining starting material was 36% 11, and 64% 8 (nearly equal amounts of erythro and threo) after 40 min. No 1 was observed, but the hydrolysis product, ethyl crotonate, was observed. Thus, in the presence of catalyst, the reaction of 1 and benzaldehyde is reversible. But, at the catalyst level (0.3%) used in the studies of the Reformatsky-type reaction, the reverse process appears to be slow, and isomerization of 8 to 11 leads to mixtures of 8 and 11 with far lower 11 content than the >96% obtained in the Reformatsky-type reaction at the same temperature. When the catalyst concentration is increased threefold, the reverse Reformatsky-type reaction proceeds further, but isomerization of 8 to 11 is still incomplete. Apparently, the catalyst becomes deactivated after a relatively short period of time. Similar catalyst deactivation was reported for the bifluoride-catalyzed isomerization of silyl ketene acetals.[14b] It does not appear that the temperature-dependent regioselectivity of the reaction of 1 with benzaldehyde is due to a catalyzed reverse reaction of 8 and 11 or a catalyzed isomerization of 8 to 11 since these processes seem to be much slower than the product-determining processes.

Conclusions

Analysis of the marked temperature dependence of the regiochemistry of the anion-catalyzed Reformatsky-type reaction of aldehydes with silyl ester dienolates leads to the conclusion that product composition is determined predominantly by a dissociative mechanism at room temperature. A nondissociative mechanism may contribute at low temperature. The silyl polyenolates 1, 2, and 3 are obtained predominantly as the thermodynamic Z isomers even under conditions which, for silyl ketene acetals, are nonequilibrating. Facile E/Z equilibration of 1 occurs under the influence of anion catalysts.

Experimental Section

Materials and Methods. Tetrahydrofuran (THF) was purified by distillation over sodium–benzophenone just prior to use. Tris(dimethylamino)sulfonium bifluoride ($TASHF_2$) was prepared and purified as described earlier.[14b] Benzaldehyde was purchased from Aldrich Chemical Co. and distilled prior to use. Tetrabutylammonium acetate was purchased from Fluka Chemical Co. and dried at 0.02 Torr for 24 h prior to preparation of a standard solution in THF. ^1H NMR spectra were recorded with a Nicolet 360WB spectrometer, GC analyses were performed with a Hewlett-Packard 5890A chromatograph, and GC/MS data were obtained with a Varian 3700 GC with a V.G. Micromass 16-F mass spectrometer.

1-Ethoxy-1-(trimethylsiloxy)-1,3-butadiene (1) (90% *Z*, 10% *E*). To a solution of 168.3 g (233 mL, 1.66 mol) of diisopropylamine in 1.6 L of THF at 0 °C was added 1.66 mol of 1.6 M butyllithium in hexane. After 30 min at 0 °C, the solution was cooled to −78 °C, and 185.2 g (1.16 mol) of ethyl 3-butenoate was added at a rate to maintain a temperature below −70 °C. After 30 min 185.4 g (216 mL, 1.71 mol) of chlorotrimethylsilane was added, and the mixture was allowed to warm to room temperature. The mixture was filtered under argon, the filtrate was evaporated, treated with hexane, and filtered under argon, and the filtrate was concentrated and distilled in a spinning-band column to give 157 g of 1[1] in several fractions, with the composition ranging from 75% Z in an early fraction to 90% Z in the final fraction, bp 44–51 °C/2 Torr. Anal. (90% Z) Calcd for $C_9H_{18}O_2Si$: C, 58.02; H, 9.74; Si, 15.07. Found: C, 57.75; H, 9.63; Si, 14.64. IR (CCl_4, cm^{-1}): 1645 (conj C=C), 1250, 850 (Si-CH_3), 1215 (=C-O). UV (isooctane): 247 nm (ϵ 20300). ^1H NMR of 1 (90% Z, 10% E) in $CDCl_3$ (δ, J (Hz)): Z isomer, 0.24 (s, 9 H, $SiCH_3$), 1.30 (t, J = 7, 3 H, CH_3), 3.80 (q, J = 7, 2 H, OCH_2), 4.45 (d, J = 10, 1 H, =CH-2), 4.58 (m, ^3J = 10, ^2J = 2, ^3J = 1, 1 H, =CH-4), 482 (dd, ^3J = 18, ^2J = 2, 1 H, =CH-4), 6.50 (dt, ^3J = 18, ^3J = ^3J = 10, 1 H, =CH-3); E isomer, 0.27 (s, 9 H, $SiCH_3$), 1.245 (t, J = 7, 3 H, CH_3), 3.91 (q, J = 7, 2 H, OCH_2), 4.54 (d, J = 10, 1 H, =CH-2), 4.58 (m, ^3J = 10, ^2J = 2, ^3J = 1, 1 H, =CH-4), 4.82 (dd, ^3J = 18, ^2J = 2, 1 H, =CH-4), 6.5 (dt, ^3J = 18, ^3J = ^3J = 10, 1 H, =CH-3). NOE: Irradiation at 0.24 ppm enhanced 6.5 ppm, irradiation at 4.45 ppm enhanced 3.8 ppm, irradiation at 3.8 ppm enhanced 4.45 ppm.

Equilibration of 1 with Mercuric Iodide. A solution of 75% Z 1 in benzene-d_6 saturated with mercuric iodide was analyzed by ^1H NMR after 4 days and found to contain 1 (89% Z, 11% E) as well as polymer (broad peaks) and ethyl 3-butenoate.

Equilibration of 1 with Tris(*N*-piperidinyl)sulfonium Bifluoride ($TPSHF_2$). To a solution of 55 μL of 1 (75% Z, 25% E) in 1 mL of THF-d_8 was added 25 μL of $TPSHF_2$[18] (0.1 M in THF-d_8), leading to immediate formation of a yellow color. The ^1H NMR spectrum measured after 44 min showed 36% ethyl crotonate and 64% 1 (91% Z, 9% E). The E/Z composition of 1 was unchanged after an additional 30 h. A similar experiment performed with 1 (89% Z, 11% E) led to formation of 13% ethyl crotonate and 87% 1 (90% Z, 10% E) as determined by ^1H NMR after 53 min. A similar experiment using 2 (67% Z) resulted in no change of the E/Z composition (13% hydrolysis was observed). A similar experiment using 3 (95% Z) resulted in 30% hydrolysis, but no change in the stereochemistry of 3.

1-Ethoxy-1-(trimethylsiloxy)-2-methyl-1,3-butadiene (2) (67% *Z*, 33% *E*). The procedure of Savard and Brassard[20] was used for the preparation of 2 (67% Z), bp 45–46 °C/1.6 Torr. Anal. Calcd for $C_{10}H_{20}O_2Si$: C, 59.95; H, 10.06; Si, 14.02; m/z 200.1232. Found: C, 59.49; H, 9.60; Si, 13.57; m/z 200.1244. ^1H NMR ($CDCl_3$, δ, J (Hz)): Z isomer, 0.23 (s, 9 H, $SiCH_3$), 1.24 (t, J = 7, 3 H, CH_3), 1.68 (s, 3 H, =CCH_3), 3.85 (q, J = 7, 2 H, OCH_2), 4.78 (dd, ^3J = 10.6, ^2J = 2, 1 H, =CH-4), 4.845 (dd, ^3J = 18, ^2J = 2, 1 H, =CH-4), 6.64 (dd, ^3J = 18, ^3J = 10.6, 1 H, =CH-3); E isomer, 0.23 (s, 9 H, $SiCH_3$), 1.24 (t, J = 7, 3 H, CH_3), 1.63 (s, 3 H, =CCH_3), 3.84 (q, J = 7, 2 H, OCH_2), 4.76 (dd, ^3J = 10.6, ^2J = 2, 1 H, =CH-4), 4.83 (dd, ^3J = 18, ^2J = 2, 1 H, =CH-4), 6.80 (dd, ^3J = 18, ^3J = 10.6, 1 H, =CH-3). NOE: Irradiation at 0.23 ppm enhanced 1.63 ppm resonance of major isomer.

Methyl 2-Methyl-4-(trimethylsilyl)-2-butenoate (4). LDA was prepared as for 1 from 0.673 mol of butyllithium, and at −78 °C 117 mL (0.675 mol) of hexamethylphosphoramide was added followed by 75 g (0.657 mol) of methyl tiglate and 87.7 mL (0.69 mol) of chlorotrimethylsilane. Workup similar to that for 1 gave 65.6 g of 4, bp 50 °C/0.35 Torr. Since the product contained a small amount of HMPA, it was dissolved in hexane and washed twice with cold water, dried ($MgSO_4$), and redistilled. Anal. Calcd for $C_9H_{18}SiO_2$: C, 58.02; H, 9.74; Si, 15.07; m/z 186.1076. Found: C, 57.42; H, 9.53; Si, 15.94; m/z 186.1088. ^1H NMR ($CDCl_3$, δ, J (Hz)): 0.01 (s, 9 H, $SiCH_3$), 1.66 (d, J = 10, 2 H, $SiCH_2$), 1.74 (d, J = 1.8, 3 H, =CCH_3), 3.68 (s, 3 H, OCH_3), 6.9 (m, ^3J = 10, ^4J = 1.8, 1 H, =CH).

1-Ethoxy-1-(trimethylsiloxy)-1,3,5-hexatriene (3) (95% *Z,E*, 5% *E,E*). With the procedure for the preparation of 1, 204 g (1.456 mol) of ethyl 3,5-hexadienoate (conveniently prepared by the reaction of sorbic acid chloride with ethanol and triethylamine) was converted to 97.3 g of 3, bp 49 °C/0.1 Torr. Anal. Calcd for $C_{11}H_{20}SiO_2$: C, 62.21; H, 9.49; Si, 13.23; m/z 212.1232. Found: C, 61.40; H, 9.53; Si, 12.34; m/z 212.1228. UV (cyclohexane): 288 nm (ϵ 18600). ^1H NMR ($CDCl_3$, δ, J (Hz)): Z,E isomer, 0.26 (s, 9 H, $SiCH_3$), 1.31 (t, J = 7.5, 3 H, CH_3), 3.825 (q, J = 7.5, 2 H, OCH_2), 4.46 (d, J = 10, 1 H, =CH-2), 4.825 (dd,

^3J = 10, ^2J = 2, 1 H, =CH-6), 4.96 (dd, ^3J = 17, ^2J = 2, 1 H, =CH-6), 5.95 (dd, J = 15, 10, 1 H, =CH-4), 6.375 (ddd, J = 17, 10, 10, 1 H, =CH-5), 6.415 (dd, J = 15, 10, 1 H, =CH-3); *E,E* isomer, 0.28 (s, 9 H, $SiCH_3$), 1.265 (t, J = 7.5, 3 H, CH_3), 3.94 (q, J = 7.5, 2 H, OCH_2), 4.54 (d, J = 10, 1 H, =CH-2) (the remainder of the *E,E* spectrum did not differ from that of the *Z,E* isomer).

General Procedure for Reaction of 1, 2, and 4 with Aldehydes. To a solution of 0.31 mL (3 mmol) of benzaldehyde and 10 μL of $TASHF_2$ (1 M in acetonitrile) in 30 mL of THF in a cooling bath maintained at the desired temperature was added 3 mmol of the organosilane (**1**, **2**, or **4**) by means of a syringe at such a rate that a constant temperature was maintained. After the desired reaction time (30 min at −95 °C, 20 min at −30 to −50 °C, 15 min at 0 °C or above) the reaction was quenched by addition of 3 mL of a solution of 10 mL of concentrated hydrochloric acid in 90 mL of methanol. After standing for 15 min at room temperature, the solution was added to cold saturated aqueous ammonium chloride, and the organic layer was diluted with ether, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in dichloromethane and washed with brine, dried ($MgSO_4$), and evaporated to an oil. The yield reported in Table I was estimated from the amount of unreacted benzaldehyde detected in the NMR spectrum. Analysis of the product mixture was by ^1H NMR (360 MHz) with reference to the reported spectra of *erythro*- and *threo*-methyl 2-(α-hydroxybenzyl)-3-butenoate[29] and methyl 5-hydroxy-5-phenyl-2-pentenoate.[30] GC analysis of the product mixtures was performed by using a HP 5890A gas chromatograph with a 5% phenylmethylsilicone 0.5-μm film capillary column (25 m × 0.2 mm i.d.) with a 150 °C injection port, 150 °C initial temperature, 250 °C final temperature, and 10 °C/min heating rate. Erythro and threo isomers of α adducts were barely separated, and were followed by γ adducts about 2 min later. The accuracy of the GC measurements are estimated to be ±3%.

Reaction of Dienolate 9 with Benzyl Bromide. To a stirred suspension of 870 mg (3.15 mmol) of TASF in 30 mL of THF at −78 °C was added 0.66 mL (3 mmol) of **1** (90% *Z*) while maintaining a temperature of less than −70 °C. A deep yellow color formed. After 15 min at −78 °C, 15 mL of anhydrous ether was added below −70 °C. A vacuum was applied, and the mixture was allowed to warm to −41 °C until the volume of condensate in a −100 °C cold trap was 18.8 mL. Then the mixture was cooled to −100 °C, and 0.42 mL (3.5 mmol) of benzyl bromide was added rapidly, causing the yellow color to fade. The mixture was allowed to warm to −40 °C and was then poured into cold, saturated aqueous ammonium chloride. The organic layer was separated, dried ($MgSO_4$), and evaporated. The residue was dissolved in dichloromethane, washed with brine, dried ($MgSO_4$), and evaporated to 0.5 g of oil. ^1H NMR showed 92% ethyl 2-benzyl-3-butenoate (**13**) and 8% ethyl 2-benzyl-2-butenoate (**14**). ^1H NMR (THF-d_8, δ, J (Hz)): **13**, 1.12 (t, J = 7, 3 H, CH_3), 2.81 (dd, ^2H = 13.5, ^3J = 7, 1 H, $ArCH_2$), 3.05 (dd, ^2J = 13.5, ^3J = 8, 1 H, $ArCH_2$), 3.31 (dddt, J = 7, 8, 8.5, ^4J = 1, ^4J = 1, 1 H, CH-2), 4.03 (q, J = 7, OCH_2), 5.04 (ddd, ^3J = 17, ^4J = 1, ^2J = 1, 1 H, =CH_2), 5.06 (ddd, ^3J = 10.5, ^4J = 1, ^2J = 1, 1 H, =CH_2), 5.87 (ddd, J = 17, 10.5, 8.5, 1 H, =CH-3), 7.10–7.25 (m, 5 H, ArH); **14**, 1.19 (t, J = 7, CH_3), 1.86 (d, J = 7, CH_3-4), 3.05 (d, ^2J = 14, $ArCH_2$), 3.22 (d, ^2J = 14, $ArCH_2$), 4.19 (q, J = 7, OCH_2), 6.98 (q, J = 7, =CH-3). Irradiation of the 3.05 ppm resonance caused the 3.22 ppm doublet to collapse to a singlet. Irradiation of the 1.86 ppm methyl doublet caused the 6.98 ppm quartet to collapse to a singlet. GC/MS showed two components with mass 204 (87% **13**, 10% **14** at 12.8 and 14.1 min, respectively) and a component of mass 294 (3%, 25.4 min) containing two benzyl groups. An aliquot of the contents of the cold trap was treated with hexafluorobenzene as an internal standard, and ^{19}F NMR analysis showed that 70% of the theoretical quantity of fluorotrimethylsilane had been collected in the cold trap.

Stability of Ethyl 2-(α-(Trimethylsiloxy)benzyl)-3-butenoate (8) to Bifluoride at 25 °C. To a solution of 0.3 mL (3 mmol) of benzaldehyde and 100 μL of $TPSHF_2$[18] (0.1 M in THF-d_8) in 30 mL of THF at −95 °C was added 0.66 mL (3 mmol) of **1** (90% *Z*). After 30 min at −95 °C, the reaction was quenched and worked up as in the general procedure to give 0.65 g of oil. GC analysis showed 92% ethyl 2-(α-hydroxybenzyl)-3-butenoate (**15**), and 8% ethyl 5-hydroxy-5-phenyl-2-pentenoate (**16**) (m/z 220.1085, calcd for $C_{13}H_{16}O_3$ 220.1099). ^1H NMR analysis confirmed the composition and showed approximately 53% *erythro*-**15** and 47% *threo*-**15**. The oil was dissolved in 5 mL of dichloromethane and treated with 1 mL of triethylamine and 0.5 mL of chlorotrimethylsilane. After 10 min the mixture was washed well with brine, dried ($MgSO_4$), and evaporated. The residue was dissolved in petroleum ether, filtered, and evaporated to 0.28 g of oil. ^1H NMR showed 92% ethyl 2-(α-(trimethylsiloxy)-benzyl)-3-butenoate (**8**) (53% erythro, 47% threo) and 8% ethyl 5-(trimethylsiloxy)-5-phenyl-2-pentenoate (**11**). ^1H NMR ($CDCl_3$, δ, J (Hz)): *erythro*-**8**, −0.01 (s, $SiCH_3$), 1.05 (t, J = 7, CH_3), 3.24 (dd, J = 9.5, 6.6, CHC=O), 3.96 (q, J = 7, OCH_2), 4.98 (d, J = 18, =CH-4), 5.00 (d, J = 6.6, ArCH), 5.13 (d, J = 10.5, =CH-4), 5.99 (ddd, J = 18, 10.5, 9.5, =CH-3), 7.2–7.3 (m, ArH); *threo*-**8**, −0.05 (s, $SiCH_3$), 1.28 (t, J = 7, CH_3), 3.33 (dd, J = 9.5, 9.5, CHC=O), 4.16 (q, J = 7, OCH_2), 4.84 (d, J = 18, =CH-4), 4.87 (d, J = 9.5, ArCH), 4.92 (d, J = 10.5, =CH-4), 5.45 (ddd, J = 18, 10.5, 9.5, =CH-3), 7.2–7.3 (m, ArH); **11**, −0.01 (s, $SiCH_3$), 1.26 (t, J = 7, CH_3), 2.53 (m, CH_2-4), 4.14 (q, J = 7, OCH_2), 4.74 (m, CH-5), 5.82 (dt, J = 16, 1, =CH-2), 6.88 (dt, J = 16, 7, =CH-3), 7.2–7.3 (m, ArH).

To a solution of 29 mg (0.1 mmol) of a mixture of **8** (92%) and **11** (8%) in 1 mL of THF-d_8 was added 30 μL of $TPSHF_2$ (0.01 M in THF-d_8), producing a faint yellow color. The ^1H NMR spectrum measured after 45 min showed 5.5% of benzaldehyde, and the starting material consisted of 20% **11** and 80% **8** (nearly equal amounts of erythro and threo). This composition was essentially unchanged after 18 h. In a similar experiment in which 90 μL of $TPSHF_2$ (0.01 M in THF-d_8) was used, the ^1H NMR spectrum measured after 40 min showed 30% of benzaldehyde, and the starting material consisted of 36% **11** and 64% **8** (nearly equal amounts of erythro and threo). In addition, ethyl crotonate was identified.

Analysis of Reaction Product of 2 and Benzaldehyde (Entry 16 of Table I). ^1H NMR (acetone-d_6, D_2O, δ, J (Hz)): ethyl 2-methyl-5-hydroxy-5-phenyl-2-pentenoate (56%), 1.27 (t, J = 7, 3 H, CH_3), 1.78 (d, ^4J = 1.5, 3 H, =CCH_3), 2.64 (m, 2 H, CH_2-4), 3.81 (broad s, OH), 4.16 (q, J = 7, 2 H, OCH_2), 4.85 (t, J = 5, 1 H, CH-5), 6.88 (tq, ^3J = 7, ^4J = 1.5, 1 H, =CH-3), 7.25–7.48 (m, 5 H, ArH); *erythro*-ethyl 2-methyl-2-(α-hydroxybenzyl)-3-butenoate (19%), 1.16 (s, 3 H, CH_3), 1.28 (t, J = 7, 3 H, CH_3), 4.14 (q, J = 7, 2 H, OCH_2), 4.96 (dd, ^3J = 17, ^2J = 1.5, 1 H, =CH-4), 5.12 (s, 1 H, ArCH), 5.17 (dd, ^3J = 10, ^2J = 1.5, 1 H, =CH-4), 6.40 (dd, J = 18, 10, 1 H, =CH-3), 7.25–7.48 (m, 5 H, ArH); *threo*-ethyl 2-methyl-2-(α-hydroxybenzyl)-3-butenoate (25%), 1.21 (s, 3 H, CH_3), 1.25 (t, J = 7, 3 H, CH_3), 4.19 (q, J = 7, 2 H, OCH_2), 4.93 (dd, ^3J = 17, ^2J = 1.5, 2 H, =CH-4), 5.07 (dd, ^3J = 10, ^2J = 1.5, 1 H, =CH-4), 5.19 (s, 1 H, ArCH), 6.03 (dd, J = 18, 10, 1 H, =CH-3), 7.25–7.48 (m, 5 H, ArH).

Methyl 2-Methyl-5-hydroxy-5-phenyl-2-pentenoate. To a solution of 2.07 mL (20 mmol) of benzaldehyde in 40 mL of THF was added 0.3 mL of $TASHF_2$ (1 M in acetonitrile) followed by 4.14 mL (20 mmol) of methyl 4-(trimethylsilyl)-2-butenoate (**4**), maintaining a temperature of about 35 °C. Treatment with cold saturated ammonium chloride solution and hexane gave 5.2 g of methyl 2-methyl-5-phenyl-5-(trimethylsiloxy)-2-pentenoate as an oil. IR (CCl_4): 1715 (conj ester), 1650 cm^{-1} (C=C). ^1H NMR (acetone-d_6, δ, J (Hz)): 0.09 (s, 9 H, $SiCH_3$), 1.79 (d, J = 2, 3 H, =CCH_3), 2.55–2.7 (m, 2 H, CH_2), 3.7 (s, 3 H, OCH_3), 4.95 (2 d, J = 7, 1 H, OCH), 6.855 (tq, ^3J = 7, ^4J = 2, 1 H, =CH), 7.25–7.5 (m, 5 H, ArH). Hydrolysis of 3 g of the product with methanolic hydrochloric acid gave 2.1 g of methyl 2-methyl-5-hydroxy-5-phenyl-2-pentenoate as an oil. IR (CCl_4): 3610, 3490 (OH), 1715 (conj ester), 1650 cm^{-1} (C=C). ^1H NMR (acetone-d_6, δ, J (Hz)): 1.88 (d, J = 2, 3 H, =CCH_3), 2.55–2.65 (m, 2 H, CH_2), 3.47 (s, 3 H, OCH_3), 4.45 (m, 1 H, OCH), 6.14 (tq, ^3J = 6, ^4J = 2, 1 H, =CH). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.89; H, 7.19.

Methyl 2-Methyl-5-hydroxy-5-(4-nitrophenyl)-2-pentenoate and Methyl 2-Methyl-2-(α-hydroxy-*p*-nitrobenzyl)-3-

(29) (a) Maruoka, K.; Hashimoto, S.; Kitagawa, Y.; Yamamoto, H.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3301. (b) Boldrini, G. P.; Savoia, D.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Org. Chem.* **1983**, *48*, 4108.

(30) Dugger, R. W.; Heathcock, C. H. *J. Org. Chem.* **1980**, *45*, 1181.

butenoate. The preceding procedure was used with *p*-nitrobenzaldehyde instead of benzaldehyde, and the reaction temperature was maintained at −30 °C. The reaction mixture was quenched at −30 °C with methanolic hydrochloric acid to provide the mixture of hydroxy esters directly as an oil consisting of 76% of the methyl 2-pentenoate and 24% of the methyl 3-butenoate (65% threo, 35% erythro) as determined by NMR analysis. Upon standing, crystalline methyl 2-methyl-5-hydroxy-5-(4-nitrophenyl)-2-pentenoate separated. After two recrystallizations from toluene the melting point was 73–74 °C. ^{1}H NMR (acetone-d_6, D_2O, δ, J (Hz)): 1.74 (d, ^4J = 1.5, 3 H, CH_3), 2.68 (m, 2 H, CH_2-4), 3.40 (s, 1 H, OH), 3.68 (s, 3 H, OCH_3), 5.05 (t, J = 6, 1 H, CH-5), 6.86 (tq, ^3J = 7, ^4J = 1.5, 1 H, =CH-3), 7.72 (d, J = 8, 2 H, ArH), 8.24 (d, J = 8, 2 H, ArH). Anal. Calcd for $C_{13}H_{15}O_5N$: C, 58.86; H, 5.70, N, 5.28. Found: C, 58.88, H, 5.45; N, 5.07. The supernatant oil consisted of 45% γ adduct, 19% erythro α adduct, and 36% threo α adduct as determined from the ^{1}H NMR spectrum (in acetone-d_6, D_2O, δ, J (Hz)): *erythro*-methyl 2-methyl-2-(α-hydroxy-*p*-nitrobenzyl)-3-butenoate, 1.15 (s, 3 H, CH_3), 3.40 (s, 1 H, OH), 3.70 (s, 3 H, OCH_3), 4.95 (dd, ^3J = 18, ^2J = 1.5, 1 H, =CH-4), 5.18 (dd, ^3J = 11, ^2J = 1.5, 1 H, =CH-4), 5.25 (s, 1 H, ArCH), 6.37 (dd, J = 18, 11, 1 H, =CH-3), 7.61 (d, J = 8, 2 H, ArH), 8.19 (d, J = 8, 2 H, ArH); threo isomer, 1.16 (s, 3 H, CH_3), 3.40 (s, 1 H, OH), 3.74 (s, 3 H, OCH_3), 4.94 (dd, ^3J = 18, ^2J = 1, 1 H, =CH-4), 5.12 (dd, ^3J = 11, ^2J = 1, 1 H, =CH-4), 5.34 (s, 1 H, ArCH), 6.17 (dd, J = 18, 11, 1 H, =CH-3), 7.62 (d, J = 8, 2 H, ArH), 8.18 (d, J = 8, 2 H, ArH).

Reaction of 4 with Acetic Acid-*d*. To a solution of 0.1 mL (0.5 mmol) of **4** in 0.8 mL of THF-d_8 were added 30 μL of acetic acid-*d* and 50 μL of tetrabutylammonium acetate (0.1 M in THF-d_8). The ^{1}H NMR spectrum of the solution after 2 days showed 93% unchanged **4** and 7% methyl 2-deuterio-2-methyl-3-butenoate: 1.14 (t, J_d = 1, 1 H, $CDCH_3$), 3.50 (s, 3 H, OCH_3), 4.97 (dd, ^3J = 10, ^2J = 2, 1 H, =CH_2), 5.03 (dd, ^3J = 17, ^2J = 2, 1 H, =CH_2), 5.84 (ddt, J = 17, 10, J_d = 1, 1 H, =CH).

Reaction of 3 with Methanol-*d*. To a solution of 0.12 mL (0.5 mmol) of **3** in 0.8 mL of THF-d_8 was added 50 μL of tetrabutylammonium acetate (0.1 M in THF-d_8). The ^{1}H NMR spectrum of the solution showed 67% ethyl 3,5-hexadienoate-2-*d* (1.21 (t, J = 7, CH_3), 3.03–3.08 (m, 0.6 H, CHD), 4.08 (q, J = 7, 2 H, OCH_2), 4.99 (dd, ^3J = 10, ^2J = 2, 1 H, =CH_2), 5.11 (dd, ^3J = 17, ^2J = 2, 1 H, =CH_2), 5.77 (dtt, J = 15, 7, J_d = 1, 1 H, =CH-3), 6.14 (dd, J = 15, 10, 1 H, =CH-4), 6.32 (ddd, J = 17, 10, 10, 1 H, =CH-5)) and 33% ethyl sorbate-2-*d* (1.23 (t, J = 7, 3 H, CH_3), 1.82 (d, J = 5.5, 3 H, CH_3), 4.12 (q, J = 7, 2 H, OCH_2), 6.14 (dd, J = 16, 5.5, 1 H, =CH-5), 6.23 (dd, J = 16, 10, 1 H, CH-4), 7.21 (dd, J = 15, 10, 0.5 H, =CH-3 adjacent to =CH-2), 7.20 (dt, J = 10, J_d = 2, 0.5 H, =CH-3 adjacent to =CD-2)).

Acknowledgment. We are grateful to T. Fukunaga, T. V. RajanBabu, B. E. Smart, B. M. Trost, and O. W. Webster for helpful discussions of this work. The thoughtful suggestions of one of the referees are appreciated, and the assistance of R. S. Peacock and K. M. Stoltzfus in the experimental work is gratefully acknowledged.

Registry No. (*Z*)-**1**, 114996-00-8; (*E*)-**1**, 114996-01-9; (*Z*)-**2**, 114996-02-0; (*E*)-**2**, 114996-03-1; (*Z*,*E*)-**3**, 114996-05-3; (*E*,*E*)-**3**, 114996-06-4; **4**, 114996-04-2; **5**, 114996-14-4; **13**, 39149-91-2; **14**, 114996-13-3; TASF, 59218-87-0; ethyl 3-butenoate, 1617-18-1; methyl tiglate, 6622-76-0; ethyl 3,5-hexadienoate, 81838-64-4; sorbic acid chloride, 2614-88-2; benzaldehyde, 100-52-7; ethyl 5-hydroxy-5-phenylpent-2-enoate, 114996-07-5; ethyl 2-(hydroxyphenylmethyl)but-3-enoate, 89922-39-4; ethyl 5-hydroxy-2-methyl-5-phenylpent-2-enoate, 114996-08-6; ethyl 2-(hydroxyphenylmethyl)-2-methylbut-3-enoate, 114996-09-7; methyl 5-hydroxy-2-methyl-5-phenylpent-2-enoate, 92186-72-6; methyl 2-(hydroxyphenylmethyl)-2-methylbut-3-enoate, 92186-70-4; methyl 5-hydroxy-5-(4-nitrophenyl)-2-methylpent-2-enoate, 108733-47-7; methyl 2-(hydroxy(4-nitrophenyl)methyl)-2-methylbut-3-enoate, 114996-10-0; *p*-nitrobenzaldehyde, 555-16-8; ethyl 5-hydroxy-5-(4-nitrophenyl)pent-2-enoate, 114996-11-1; ethyl 2-(hydroxy(4-nitrophenyl)methyl)but-3-enoate, 114996-12-2; ethyl 3,5-hexadienoate-2-*d*, 114996-15-5; ethyl sorbate-2-*d*, 114996-16-6.

Palladium- and Nickel-Catalyzed Reaction of Trimethylsilyl Cyanide with Acetylenes. Addition of Trimethylsilyl Cyanide to the Carbon–Carbon Triple Bonds[1]

Naoto Chatani,* Takumi Takeyasu, Nobuhiko Horiuchi, and Terukiyo Hanafusa

The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567, Japan

Received December 11, 1987

The reaction of trimethylsilyl cyanide (**1**) with acetylenes in the presence of a transition-metal complex was investigated. The structures of starting acetylenes and catalysts and both amounts of solvent and **1** highly affected product distributions. The $PdCl_2$/pyridine catalyzed reaction of phenylacetylene and para-substituted phenylacetylenes with **1** resulted in the addition of **1** to the carbon–carbon triple bonds to give cyano-substituted vinylsilanes in good to high yields with high regio- and stereoselectivity. Ortho-substituted phenylacetylenes gave addition products less stereoselectively. Stereoselectivity affording *Z* adducts decreased in the order of para- > meta- > ortho-substituted phenylacetylenes. The $NiCl_2$/DIBAH-catalyzed reaction of arylacetylenes was less stereoselective regardless of substitution patterns of arylacetylenes used. When the nickel-catalyzed reaction of arylacetylenes was run without solvent using an excess amount of **1**, 5-amino-1*H*-pyrrole-2-carbonitriles were obtained as a single product, instead of the above simple addition products. The reaction of terminal aliphatic acetylenes with **1** also gave addition products with moderate stereoselectivity. Internal acetylenes gave complex mixtures including addition products and/or pyrrole derivatives. Diarylacetylenes afforded 5-amino-1*H*-pyrrole-2-carbonitriles selectively in the presence of a palladium or nickel catalyst (without solvent and an excess amount of **1**). Intramolecular cyclization of a 1,6-diyne was also studied.

In recent years, vinylsilanes have played an ever increasing role in synthetic organic chemistry.[2,3] For their potential utility, much attention has been focused on exploring synthetic methods of functionalized vinylsilanes.

0022-3263/88/1953-3539$01.50/0