1-Acetoxy-1,3-bis(trimethylsilyl)prop-2-ene. A Synthon for a Propenyl 1,3-Dipole in Diene Synthesis

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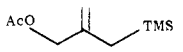
The title reagent undergoes molybdenum-catalyzed alkylation by which it demonstrates its cationic nature. Trimethylsilyl trifluoromethanesulfonate induces direct olefination with aromatic acetals to give (*E,E*)-1,3-dienes. Fluoride ion serves as a nucleophilic trigger to effect carbonyl addition and elimination with aldehydes to give the (*E,E*)- and (*E,Z*)-1,3-dienes. Thus, a 1,3-bis(silyl)alkene can serve as a very mild olefination agent in which one C–Si bond serves as the nucleophile for carbonyl addition and the second C–Si bond as the initiation for vicinal elimination in a single operation.

The development of bifunctional reagents such as **1** for synthesis holds the promise of great versatility in building complex structures. In such conjunctive reagents, nu-



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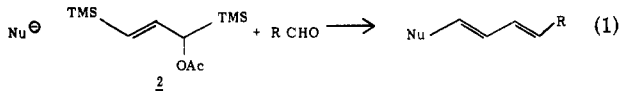
cleophilic and electrophilic centers must have their reactivity so attuned that they may coexist. Silyl acetates form a convenient class since they are easily available and very stable. Of course, the stability creates a problem of sufficient reactivity to exercise their nucleophilic and electrophilic properties. While the conditions to express the nucleophilic properties of allylsilanes are, by now, well established,[4] the expression of the electrophilic properties of the allyl acetates has only recently been developed by using transition metals.[5]

Initially, attention focussed on cyclization reactions, but the possibility of a chain extension method using a suitably designed bifunctional reagent as a lynchpin also seems attractive (see eq 1). 1-Acetoxy-1,3-bis(trimethylsilyl)-



(1)

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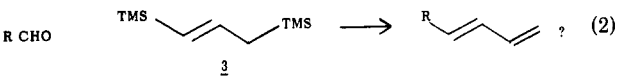
prop-2-ene (**2**)[6] is especially interesting since, after nucleophilic substitution, the resulting bis(silane) can allow direct coupling with an aldehyde to generate dienes. In this latter regard, the direct coupling of 1,3-bis(trimethylsilyl)-1-propene with aldehydes according to eq 2



(2)

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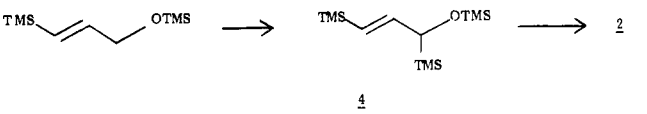
seems not to have been recorded.[7] Such a reaction would obviate the problems associated with using lithiated allyltrimethylsilane and allow condensations under more neutral conditions or by using Lewis acids. In this paper, we wish to record the successful realization of these goals which constitutes a useful diene synthesis.

Preparation and Alkylation of 2. The allyl acetate was prepared from 1-(trimethylsilyl)-3-(trimethylsiloxy)-propene by metalation and silylation (see eq 3). While



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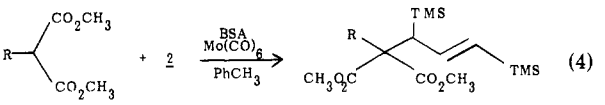
(3)

the metalation proceeded normally, the silylation appeared to be slow—a fact that led us to quench the lithiated compound at −78 °C and allow it to stir 2 h before working it up.[6] In this way **4** was isolated in 97% yield. Aqueous acid hydrolysis and acetylation gave a 96% yield of **2**.

As previously noted, palladium-catalyzed alkylation was accompanied by substantial to exclusive desilylation.[6,8,9]



(4)

5

a) R = CH_3
b) R = CH_2=$CHCH_2CH_2$
c) R = CH_2=$CHCH_2CH_2CH_2$
d) R = $(CH_3O)_2CH(CH_2)_7$

In complete contrast, molybdenum-catalyzed reactions did lead to alkylation with no trace of desilylation.[8,10] The conditions for the preparation of **5a** were optimized. A 1 M solution of **2** in toluene was reacted with 1.1 equiv of

(1) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1979**, *101*, 6429; *J. Am. Chem. Soc.* **1983**, *105*, 2315, 2326. Trost, B. M.; Chan, D. M. T.; Nanninga, T. N. *Org. Synth.* **1984**, *62*, 58. Also see: Hosomi, A.; Hashimoto, H.; Sakurai, H. *Tetrahedron Lett.* **1980**, *21*, 951. Knapp, S.; O'Connor, V.; Mobilis, D. *Tetrahedron Lett.* **1980**, *21*, 4557.

(2) Trost, B. M.; Vincent, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 5680. Trost, B. M.; Curran, D. P. *Ibid.* **1981**, *103*, 7380. Trost, B. M.; Hiemstra, H. *Ibid.* **1982**, *104*, 886. Trost, B. M.; Adams, B. *J. Am. Chem. Soc.* **1983**, *105*, 4849.

(3) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1981**, *103*, 5972; *J. Am. Chem. Soc.* **1982**, *104*, 3733. Trost, B. M.; Renaut, P. *Ibid.* **1982**, *104*, 6668. Trost, B. M.; Nanninga, T. N.; Chan, D. M. T. *Organometallics* **1982**, *1*, 1543.

(4) (a) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. (b) Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1. (c) Fleming, I. *Compr. Org. Chem.* **1979**, *3*, 539. (d) Magnus, P. D.; Sarkar, T.; Djuric, D. *Compr. Organometal. Chem.* **1982**, *7*, 515. Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: Berlin, 1983.

(5) For reviews see: Trost, B. M. *Tetrahedron* **1977**, *33*, 2615; *Acc. Chem. Res.* **1980**, *13*, 385. Trost, B. M. *Pure Appl. Chem.* **1981**, *53*, 2357. Trost, B. M. *Compr. Organometal. Chem.* **1982**, *8*, 799. Tsuji, J. "Organic Synthesis by with Palladium Compounds"; Springer-Verlag: Berlin, 1980.

(6) Trost, B. M.; Self, C. R. *J. Am. Chem. Soc.* **1983**, *105*, 5942.

(7) For the olefination of carbonyl compounds with preformed anions of allylsilanes see: Sato, F.; Uchiyama, H.; Iida, K.; Kotayashi, Y.; Sato, M. *Chem. Commun.* **1983**, 921. Chan, T. H.; Li, J. S. *Ibid.* **1982**, 969. Carter, M. J.; Fleming, I.; Percival, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2415. Yamamoto, Y.; Saito, Y.; Maruyama, K. *Chem. Commun.* **1982**, 1326. Also see: Corriu, R. J. P.; Masse, J.; Samate, D. *J. Organometal. Chem.* **1975**, *93*, 71.

(8) Trost, B. M.; Lautens, M. *Organometallics* **1983**, *2*, 1687.

(9) Also see: Trost, B. M.; Self, C. R. *J. Org. Chem.* **1984**, *49*, 468.

(10) (a) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1982**, *104*, 5543. (b) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1983**, *105*, 3343. (c) Trost, B. M.; Lautens, M. *Tetrahedron Lett.* **1981**, *22*, 4525. (d) Trost, B. M.; Yoshida, J.-I.; Lautens, M. *J. Am. Chem. Soc.* **1983**, *105*, 4494.

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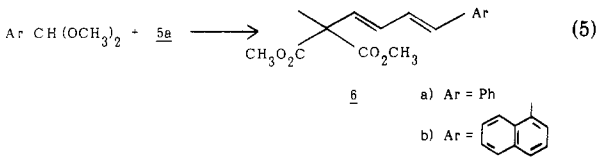
dimethyl methylmalonate and 1.1 equiv of BSA [*O,N*-bis(trimethylsilyl)acetamide] in the presence of 20 mol % of catalyst to give 70% of the desired product. When these conditions were used as standard, the other alkylated malonates were reacted to give the requisite 1,3-bis(silanes) **5**. The compounds were fully characterized as detailed in the Experimental Section.

Diene Synthesis. The condensation of allylsilanes with aldehydes can be envisioned by using either Lewis acids or fluoride ion.[4] The Lewis acid methodology seems to have been more extensively utilized. The reaction of **5** with benzaldehyde in the presence of a variety of Lewis acids led to very poor results. The higher reactivity sometimes exhibited by using acetals under Lewis acid conditions[11] led us to use benzaldehyde dimethyl acetal. Many com-



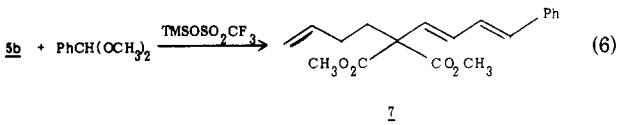
(5)

mon Lewis acids such as $AlCl_3$, BCl_3, $TiCl_4$, $SnCl_4$, and $C_2H_5AlCl_2$ gave very poor results. On the other hand, modest yields (27–44%) of exclusively the (*E,E*)-diene were obtained by using boron trifluoride etherate or trimethylsilyl triflate. The latter was preferred since it gave somewhat better results and only a *catalytic* amount was required.

The exclusive formation of the (*E*)-diene **6a** was readily discerned by a single set of ^{13}C signals in the NMR spectrum (see Experimental Section) and the coupling pattern in the ^1H NMR spectrum [δ 6.80 (ddd, J = 15.5, 8.3, 1.0, 1 H, 6.55, (d, J = 15.5, 1 H), 6.33 (dd, J = 15.5, 8.3, 1 H), 6.24 (bd, J = 15.5, 1 H)].

The dimethyl acetal of naphthaldehyde gave analogous results leading to **6b**. On the other hand, the acetals of furfural, pyridine-3-carboxaldehyde, and hexanal failed to give detectable amounts of the dienes. While the basicity of the pyridine substrate and the instability of the furan substrate explain their failure, the inability of the hexanal acetal to react is surprising.

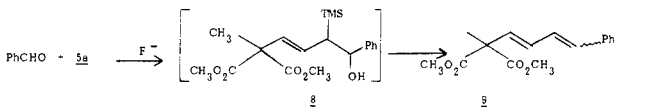
The other substituted bis(silanes) can participate within this limited range of acetals. Thus, **5b** gave a 38% yield of **7** (eq 6) using 10 mol % of trimethylsilyl triflate. In



(6)

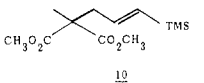
these reactions, we find it advantageous to use 1 equiv of $(C_4H_9)_2SnCl_2$ as a scavenger for adventitious acid.

With the limited success of the Lewis acid catalyzed reaction, we turned our attention to fluoride-initiated additions.[2,12] In stark contrast to the Lewis acid catalyzed reaction, tetra-*n*-butylammonium fluoride initiates addition of **5a** to the free aldehydes (see eq 7). In these re-



(7)

actions, solvent choice was critical. Increasing solvent polarity from methylene chloride to acetonitrile to dipolar aprotic solvents like DMF, HMPA, and DMI dramatically increased the rate of the reaction and yield. Most notably, the product of protodesilylation **10** decreased as the rate



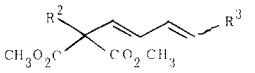
of reaction increased. For synthetic purposes, we settled upon DMI as the solvent of choice.

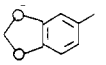
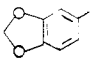
The quality of the tetra-*n*-butylammonium fluoride also affected the reaction in an unexpected fashion. Whereas, the Aldrich THF solution contains up to 5 mol % water, it gave good yields of the desired dienes and only required 10 mol %. On the other hand, a solution dried over 4A molecular sieves required up to 50 mol % before complete reaction. Obviously, a small amount of a proton source was required as a co-catalyst. Table I summarizes the generality of this diene synthesis.

Aryl aldehydes possessing electron rich (entries 3 and 5) to normal (entries 1, 2, and 8) to electron poor (entry 4) aromatic rings all participate well. On the other hand, aliphatic aldehydes give much lower yields and impure products (entries 6 and 7). The presence of α-protons apparently accounts for this limitation. Support for such an interpretation arises from the observation of enhanced protodesilylation product.

In each case, a *Z,E*:*E,E* mixture as in **9** was obtained. NMR spectroscopy allowed assignment. For example, the (*E,E*)-naphthaldehyde diene (**6b**) exhibits absorptions for the vinyl region at δ 7.4 (d, J = 15 Hz), 6.90 (dd, J = 15, 10 Hz), 6.48 (dd, J = 15.5, 10 Hz), and 6.29 (d, J = 15.5 Hz). The (*Z,E*)-diene shows an AMNY pattern analyzed as δ_{H_A} 7.00, δ_{H_M} 6.545, δ_{H_N} 6.46, and δ_{H_Y} 6.3 with J_{AM} = 10.7 Hz, J_{MN} = 10.5 Hz, J_{NY} = 15.5 Hz, and $J_{AN} = J_{AY} = J_{MY}$ = 0. The 15- and 15.5-Hz olefinic coupling constants confirm the *E,E* stereochemistry in the former and the 10.7- and 15.5-Hz couplings confirm the *Z,E* stereochemistry in the latter. Of the two (*Z,E*)-dienes **11** and **12**. the chemical shifts are in better accord with the isomer **12**. In particular, the two terminal protons appear as broadened doublets in the *E,E* and *Z,E* isomers (vide supra) where the highest field doublet is identical for both isomers and

Table I. Reaction of Bis(silanes) 5 with Aldehydes[a]

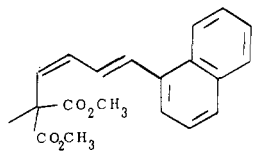


entry	bis (silane)	R^1CHO R^1	R^2	R^3	*E,Z*: *E,E*[b]	yield, %[c]
1	**5a**	Ph	CH_3	Ph	52:48	82
2	**5a**		CH_3		40:60	78
3	**5a**		CH_3		55:45	64
4	**5a**		CH_3		53:47	67
5	**5a**		CH_3		50:50	86
6	**5a**		CH_3		53:47	39[d]
7	**5a**	n-C_5H_{11}	CH_3	n-C_5H_{11}	55:45	29[d]
8	**5b**	Ph	CH_2=CHC-H_2CH_2	Ph	52:48	76

[a] Typical ratios of reactants were 0.5 mmol of **5**, 1.5 mmol of aldehyde, and 10 mol% of fluoride catalyst. [b] Ratio determined by NMR spectroscopy. [c] Yields are for isolated pure products unless otherwise noted. [d] While the analysis showed only one spot, NMR spectroscopy shows some impurities.

(11) Murata, S.; Suzuki, M.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 3248.

(12) Hosomi, A.; Shirahata, A.; Sakurai, H. *Tetrahedron Lett.* **1978**, 3043. Also see: Bennetau, B.; Dunogues, J. *Ibid.* **1983**, *24*, 4217.



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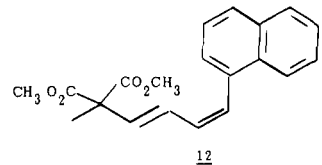

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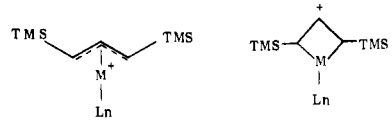
the lowest field doublet changes dramatically. In addition, the proton β to the aryl ring also shows a significant shift. The anisotropy of the double bonds and the aryl ring account for the observed trends in **12** but not **11**. By analogy, we assign the same stereochemistry to the other cases.

Discussion

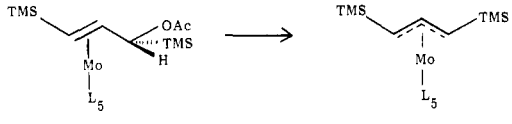
The successful use of **2** in alkylation and the subsequent condensation with aldehydes establishes the utility of this approach to synthesize highly substituted dienes. The lack of protodesilylation in the Mo-catalyzed reactions in contrast to the Pd-catalyzed reactions is noteworthy. While a detailed discussion of this phenomenon is outside the scope of this paper, it purportedly relates to the relative importance of metalocyclobutane structures such as **14** in



13 14

contrast to π-allyl structures such as **13** in contributing to the ground state.[8] Inspection of structures such as **14** reveals the reason why desilylation may become very facile in these metal-catalyzed reactions since a positive charge is on a carbon β to the silicon substituent.

Silicon should disfavor displacement reactions at the α-carbon for both electronic and steric reasons.[13] The ability of a transition metal to facilitate such reactions is another advantage of this approach. The metal initially coordinates with the olefin. Since such coordination is facilitated by a lowering of the antibonding orbitals of the olefin, as silicon substitution should achieve, the trimethylsilyl group should enhance rather than inhibit this step. The metal-assisted ionization of acetate now becomes intramolecular (see eq 8) which should minimize steric



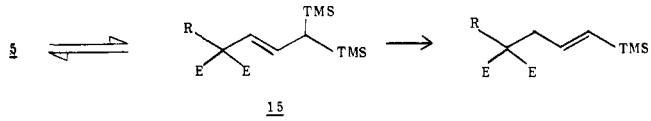
(8)

effects. Since the positive charge is largely delocalized onto the metal, any electronic destabilization of charge by silicon should also be minimized. Thus, metal-catalyzed alkylations may be a general alternative to classical displacements where structural features inhibit reaction.

The direct olefination with the 1,3-bis(silyl)propene unit is surprisingly sensitive to the nature of the electrophile and the choice of process, i.e., either a nucleophilic trigger or an electrophilic pull. The limited success of the electrophilic approach is understandable in terms of (1) the lowered nucleophilicity of the allylsilane due to the presence of strong electron-withdrawing groups and (2) the presence of Lewis basic sites on the allylsilane to compete for the coordination of the Lewis acid with the carbonyl partner. The success with aromatic acetals and the failure with aliphatic acetals can be rationalized as related to the ease of ionization to the reactive carbonium ion. In aliphatic cases, ionization may require participation by the allylsilane in a S_N2 type displacement.[14] Because of the diminished nucleophilicity of **5**, such reactions fail. In aromatic cases, ionization to the more electrophilic cation occurs and the latter is sufficiently reactive to overcome the diminished nucleophilicity of **5**.

The diminished nucleophilicity of the allylsilane could be overcome by using a nucleophilic trigger to generate the equivalent of an allyl anion. [No distinction is made as to whether a silicon "ate" complex or a free carbanion may be involved although we favor the "ate" complex.] For this process, the presence of the strong electron-withdrawing groups should be beneficial. The success of the fluoride approach compared to the Lewis acid method verifies these assumptions.

The formation of **10** as the product of protodesilylation is, at first glance, surprising in that allyl inversion did not appear to accompany the protodesilylation. The possibility that a free carbanion was involved which regioselectively protonated is conceivable but not consistent with the large body of organosilicon chemistry.[4] An alternative possibility is a fluoride-catalyzed equilibration to **15**[10d,15] followed by

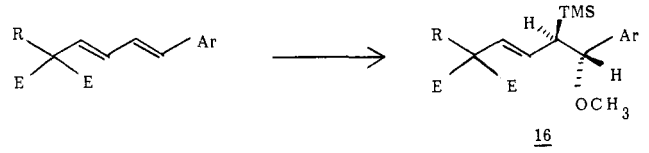


5 15

(9)

a normal protodesilylation. The correlation of the amount of protodesilylation product with the rate of the carbonyl addition supports the above interpretation. Steric hindrance at the neopentyl end of the allyl unit in **15** presumably precludes carbonyl addition at this carbon, thus accounting for only protodesilylation products from **15**.

The stereochemistry of the Lewis acid reaction is quite interesting. Using the known anti fragmentation in the Peterson olefination under Lewis acid conditions[16] suggests high diastereoselectivity in the initial addition to form the anti isomer **16**. Of the six possible open transition states



16

that can be drawn (I–VI), only IV–VI account for the deduced stereochemistry of **16**. To minimize dipole interactions, the linear conformations as represented in I and IV are generally thought to be preferred.[17] The rather severe eclipsing interaction in I between the olefin substituent and R (a type of $A_{1,3}$ strain) compared to the less severe eclipsing interaction between R and Me_3Si in IV accounts for the bias of a transition state resembling the latter. The diastereomer that results from IV, i.e., **16**, would produce the (*E*,*E*)-diene as observed.

The fluoride-initiated olefination procedure presumably involves a syn rather than an anti elimination. One of the

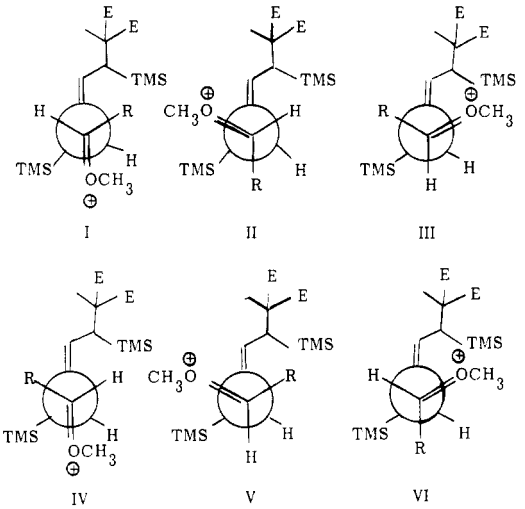
(13) For a reverse argument see 4c. For conflicting rate studies see: Eaborn, C.; Jeffrey, J. C. *J. Chem. Soc.* **1954**, 4266. Whitmore, F. C.; Sommer, L. H. *J. Am. Chem. Soc.* **1946**, *68*, 481.

(14) Cf. Johnson, W. S.; Elliott, M.; Elliott, J. D. *J. Am. Chem. Soc.* **1983**, *105*, 2904.

(15) Hosomi, A.; Shirahata, A.; Sakurai, H. *Chem. Lett.* **1978**, 901.

(16) Hudrlik, P. F.; Peterson, D. *J. Am. Chem. Soc.* **1975**, *97*, 1464.

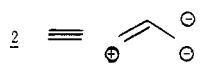
(17) Hayashi, T.; Komishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4963. Hayashi, T.; Kabeta, K.; Hamachi, I.; Kumada, M. *Tetrahedron Lett.* **1983**, *24*, 2865. Hayashi, T.; Komishi, M.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 281. Yamamoto, Y.; Yatagai, H.; Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, 102, 7107. Denmark, S. E.; Weber, E. J. *Helv. Chim. Acta* **1983**, *66*, 1655.



I II III

IV V VI

double bonds is exclusively trans; but the double bond introduced in the fragmentation of the alkoxysilane is approximately a 1:1 ratio of cis and trans. The diminished steric demands of an alkoxy anion and/or special electronic effects may account for the lack of stereoselectivity in the case of the carbonyl addition step of the fluoride-initiated reaction. The introduction of stereochemical control elements[18] may rectify this problem, a possibility that is a goal in the future. Nevertheless, the current work demonstrates the feasibility of using the bifunctional conjunctive reagent **2** as a synthon of **17** in a simple two-step operation. Most



17

interesting is the tolerance of substitution and functionality. Such chemoselectivity commends this method for the preparation of such heavily substituted systems. This selectivity derives, in part, from the dual role that silicon plays—as a nucleophilic carbanion to initiate condensation and as a nucleophilic center to effect vicinal elimination in a direct one-pot operation.[19]

Experimental Section

^{1}H NMR spectra were determined on Bruker WP200 (200 MHz) and Bruker WP270 (270 MHz) instruments. Chemical shifts were reported in δ units, part per million (ppm), downfield from tetramethylsilane. Splitting patterns were designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants (J) were reported in Hertz. ^{13}C NMR spectra were determined on a Jeolco FX-60 (60 MHz) spectrometer, with chemical shifts (δ) reported downfield relative to tetramethylsilane. Infrared spectra, were recorded on a Beckmann Acculab 7 spectrophotometer. Mass spectra were determined with either a DS-50S mass spectrometer or a Kratos DS-55 mass spectrometer. Boiling points are uncorrected. Combustion analyses were performed by Spang Microanalytical Lab., Eagle Harbor, MI, or by Galbraith Laboratories, Inc., Knoxville, TN. Thin-layer, preparative-layer, and flash chromatography silica gel was supplied by E. Merck AG Darmstadt. All solvents were dried and distilled prior to use. All reagents were used freshly distilled. Dimethyl acetals were prepared according to known general procedures.[20] All reactions were performed under nitrogen unless otherwise stated.

Alkylation of 2 with Mo(CO)$_6$ Catalysis. 1,3-Bis(trimethylsilyl)-4,4-dicarbomethoxypent-1-ene (5a). A mixture of 1.5 g (6 mmol) of 1-acetoxy-1,3-bis(trimethylsilyl)prop-2-ene[6] (**2**), 963 mg (6.6 mmol) of dimethyl methylmalonate, 1.341 g (6.6 mmol) of *O,N*-bis(trimethylsilyl)acetamide (BSA), and 316.8 mg (20 mol%) of Mo(CO)$_6$ in 6 mL of anhydrous toluene is allowed to reflux. Monitoring by TLC (hexane–10% ethyl acetate) shows the reaction is complete after 2 h. The reaction mixture is concentrated under vacuum and the residue passed through a short pad of silica gel (60–200 mesh, 30 g, eluent 10% ethyl acetate in hexane). Concentration of the organic solution gives an oil that after Kugelrohr distillation (90 °C (0.05 mmHg)) affords 1.39 g (70.2%) of **5a**.

A mixture of 732 mg (3 mmol) of **2**, 816 mg (2 equiv) of dimethyl methylmalonate, 1.250 g (6 mmol) of BSA, and 198 mg (25 mmol%) of molybdenum hexacarbonyl in 6 mL of anhydrous toluene is allowed to reflux 2 h. The reaction mixture is then diluted with hexane (300 mL), washed with water (3 × 30 mL), dried (Na_2SO_4), and concentrated. Purification of the oil residue by flash column chromatography (10% ethyl acetate in hexane) affords 792 mg of **5a** (80% yield, av 55–80%): ^{1}H NMR ($CDCl_3$) δ 5.77 (dd, J = 18, 10 Hz, 1 H), 5.53 (d, J = 18 Hz, 1 H), 3.70 (s, 3 H), 3.63 (s, 3 H), 2.43 (d, J = 10 Hz, 1 H), 1.45 (s, 3 H), 0.01 (s, 9 H), –0.017 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 172.01 s, 171.73 s, 143.49 d, 131.43 d, 55.94 s, 52.03 q, 45.59 d, 20.87 q, –0.88 q, –0.99 q; IR ($CHCl_3$) 3000 w, 1735 st, 1440 w, 1265 st, 1250 vst, 1210 st, 1140 m, 1120 m, 1000 w, 875 vst, 860 vst, 845 vst cm^{-1}; MS (70 eV), m/e (%) M$^+$ 330 (1.1) 315 (2.9), 272 (5.0), 27 (21.7), 183 (3.2), 167 (34.9), 96 (7.8), 89 (35.8), 75 (14.6), 73 (100), 59 (19.6); M_r 330.1674, found 330.1683. Anal. Calcd for $C_{15}H_{30}O_4Si_2$: C, 54.51; H, 9.15. Found: C, 54.61; H, 9.00.

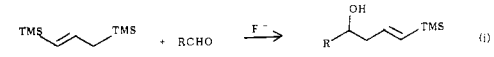
1,3-Bis(trimethylsilyl)-4,4-dicarbomethoxy-1,7-octadiene (5b). A mixture of 488 mg (2 mmol) of **2**, 409.2 mg (2.2 mmol) of dimethyl but-3-enylmalonate, 447.5 mg (2.2 mmol) of BSA, and 105.6 mg (20 mol%) of Mo(CO)$_6$ in 2 mL of anhydrous toluene is allowed to reflux 2 h. The reaction mixture is then, in part, concentrated and passed through a short pad of silica gel. Elution with 10% ethyl acetate in hexane and concentration of the organic solution gives an oil that is purified by Kugelrohr distillation (85–90 °C (0.05 mmHg)) to afford 335.3 mg (45.3% yield) of pure **5b**: ^{1}H NMR ($CDCl_3$) δ 5.63 (m, 3 H), 4.93 (m, 2 H), 3.72 (s, 3 H), 3.68 (s, 3 H), 2.37 (d, J = 8 Hz, 1 H), 1.88 (m, 4 H), 0.01 (s, 9 H), 0.048 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 171.35, 143.21, 137.70, 131.60, 114.42, 58.75, 51.92, 51.81, 44.32, 35.68, 28.69, –0.99; IR ($CHCl_3$) 3010, 2950, 2900, 1745, 1730, 1610, 1455, 1440, 1260, 1250, 1205, 1145, 1000, 875, 840 cm^{-1}; MS (70 eV), m/e (%) M$^+$ 370.1994 (0.4) (calcd for $C_{18}H_{34}O_4Si_2$ 370.1986), 355 (3.9), 315 (1.0), 311 (6.0), 257 (3.0) 146 (14.7), 132 (13.3), 107 (11.2), 89 (27.6), 73 (100), 59 (19.5); M_r 370.1986, found 370.1994. Anal. Calcd for $C_{18}H_{34}O_4Si_2$: C, 58.34; H, 9.25. Found: C, 58.92; H, 9.15.

1,3-Bis(trimethylsilyl)-4,4-dicarbomethoxy-1,8-nonadiene (5c). A mixture of 488 mg of **2**, 440 mg of dimethyl pent-4-enylmalonate (2.2 mmol), 447.5 mg (2.2 mmol) of BSA, and 105.6 mg (20 mol %) of Mo(CO)$_6$ in 2 mL of toluene is refluxed 2.5 h. The mixture is then concentrated in vacuo and passed through a short pad of silica gel, and the oil obtained is Kugelrohr distilled (100–105 °C (0.05 mmHg)) to give 347.5 mg (45.2%) of compound **5c**: ^{1}H NMR ($CDCl_3$) δ 5.63 (m, 3 H), 4.94 (m, 2 H), 3.71 (s, 3 H), 3.67 (s, 3 H), 2.37 (d, J = 9.2 Hz, 1 H), 1.85 (m, 4 H) 1.27 (m, 2 H), 0.012 (s, 9 H), –0.055 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 171.80, 143.54, 138.24, 131.61, 114.61, 58.91, 51.84, 51.73, 44.27, 35.83, 33.90, 23.57, –1.10; IR ($CHCl_3$) 3010, 2960, 2900, 1745, 1730, 1605, 1460, 1440, 1260, 1250, 1205, 1145, 1000, 875, 840 cm^{-1}; MS (30 eV), m/e (%) M$^+$ 384 (0.3), 369 (2.3), 325 (5.1), 147 (4.3), 146 (1.5), 133 (2.5) 117 (20.3), 107 (7.3), 75 (42.3), 73 (100), 59 (3.4); calcd for $C_{19}H_{36}O_4Si_2$ 384.2142, found 384.2151.

1,3-Bis(trimethylsilyl)-4,4-dicarbomethoxy-12,12-dimethoxydodec-1-ene (5d). A mixture of 732 mg (3 mmol) of **2**, 912 mg (3 mmol) of dimethyl (8,8-dimethoxyoctyl)malonate, 671.2 mg (3 mmol) of BSA, and 158.4 mg (20 mol%) of Mo(CO)$_6$ in 3

(18) Cf. Trost, B. M. *Science* **1983**, *219*, 245.

(19) After submission of this paper, a report describing the failure of diene formation with 1,3-bis(trimethylsilyl)propene and aldehydes catalyzed by fluoride ion has appeared. Corrin, R.; Escudie, N.; Guerin, C. *J. Organometal. Chem.* **1984**, *264*, 207. The observed product (see eq i) can be explained by fluoride induced silyl migration being faster than carbonyl attack or generation of an anion since the anion derived from allyltrimethylsilane is known to undergo γ attack.



(i)

(20) Meskens, F. A. *Synthesis* **1981**, 501.

mL of toluene is refluxed under nitrogen. After 8 h the reaction mixture is concentrated in vacuo and passed through a short pad of silica gel (ether eluent). The ethereal solution is then concentrated to give an oil that is purified by flash column chromatography (20% ethyl acetate in hexane) and yields 383.5 mg (26.2%) of product: ^{1}H NMR ($CDCl_3$) δ 5.64 (dd, J = 10, 18 Hz, 1 H), 5.49 (d, J = 18, 1 H), 4.31 (t, J = 5.5, 1 H), 3.70 (s, 3 H), 3.66 (s, 3 H), 3.28 (s, 6 H), 2.36 (d, J = 10, 1 H), 1.91–1.43 (m, 4 H), 1.22 (m, 10 H), 0.009 (5.9 H), −0.057 (s, 9 H); IR ($CHCl_3$) 3010, 2960, 2870, 1725, 1605, 1465, 1440, 1250, 1210, 1135, 1050, 865, 850 cm^{-1}; MS (30 eV), m/e (%) M$^+$ 488 (0.3), 441 (16.6), 397 (26.9), 315 (13.1), 285 (14.9), 132 (13.7), 107 (45.7), 89 (23.7), 75 (100), 73 (83), 59 (3.3); calcd for $C_{24}H_{48}O_6Si_2$ 488.2976, found 488.2991.

Reaction of 5 with Aldehydes Catalyzed by Tetra-*n*-butylammonium Fluoride. General Procedure. A solution of tetra-*n*-butylammonium fluoride (TBAF) (13 mg, 10 mol %) in 0.5 mL of anhydrous 1,3-dimethyl-2-imidazolidinone (DMI) (distilled over CaH_2) is placed in a flame-dried flask kept under nitrogen to which the aromatic aldehyde (0.75 mmol) is added. A solution of 0.5 mmol of bis(silane) **5** in 0.5 mL of DMI is then added dropwise (~15 min) at room temperature. For aliphatic aldehydes, a solution of 13 mg of TBAF and 0.75 mmol of the aldehyde in 0.5 mL of DMI is added dropwise (~15 min) to a solution of bis(silane) **5** in 0.5 mL of DMI stirred under nitrogen at room temperature. Coloration occurs immediately. TLC analysis reveals completion of the reaction. The reaction mixture is then diluted with water (50 mL) and extracted three times with hexane (20 mL). The combined organic layers are dried over Na_2SO_4 and concentrated in vacuo to remove all volatiles and excess aldehyde (moderate heating is necessary for less volatiles aldehydes). Purification by flash column chromatography afforded pure dienes as a mixture of *E,E* and *E,Z* isomers.

1-Phenyl-5,5-dicarbomethoxy-1,3-hexadiene (9): yield, 112.9 mg (82.3%); pale yellow oil consisting of a mixture of 1*Z*,3*Z* and 1*E*,3*E* isomers in a ratio of 52:48; ^{1}H NMR ($CDCl_3$) δ 7.30 (m, 5 H), 6.9–6.2 (m, 4 H), 3.75 (s, 6 H, *E,E* isomer), 3.72 (s, 6 H, *Z,E* isomer), 1.62 (s, 3 H, *E,E* isomer), 1.56 (s, 3 H, *Z,E* isomer); ^{13}C NMR ($CDCl_3$) δ 171.06, 136.93, 136.66, 133.30, 132.75, 131.20, 130.82, 128.95, 128.73, 128.40, 128.07, 127.30, 126.97, 126.25, 55.94, 52.86, 20.54; IR ($CHCl_3$) 3020, 2960, 1780, 1730, 1610, 1500, 1460, 1440, 1385, 1250, 1210, 1115, 995 cm^{-1}; MS (30 eV) m/e (%) M$^+$ 274 (54.2), 243 (3.8), 216 (6.4), 215 (33.7), 198 (7.3), 184 (118), 183 (100), 156 (13.1), 155 (95.1), 127 (86.7), 115 (15.7), 95 (37.8), 89 (42.1), 77 (10.5), 59 (40.2); M_r 274.1200, found 274.1205. Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.04; H, 6.61. Found: C, 69.94; H, 6.66.

1-(1-Naphthyl)-5,5-dicarbomethoxy-1,3-hexadiene (6b and 12): yield, 126.2 mg (77.8%); pale yellow oil consisting of a mixture of 1*E*,3*E* and 1*Z*,3*E* isomers in a ratio of 60:40; ^{1}H NMR ($CDCl_3$) δ 8.18–7.31 (m, 8 H), 7.05–6.81 (m, 1 H), 6.57–6.26 (m, 2 H), 3.79 (s, 6 H, *E,E* isomer), 3.70 (s, 6 H, *Z,E* isomer), 1.70 (s, 3 H, *E,E* isomer), 1.49 (s, 3 H, *Z,E* isomer); ^{13}C NMR ($CDCl_3$) δ 170.9, 170.8, 130.0, 137.7, 133.3, 132.9, 132.4, 132.1, 131.4, 131.0, 130.8, 130.6, 130.0, 129.4, 129.0, 128.2, 127.5, 126.8, 125.5, 124.8, 123.1, 55.7, 52.8, 20.4; IR ($CHCl_3$) 3030, 2960, 1785, 1740, 1600, 1515, 1465, 1440, 1380, 1260, 1200, 1110, 990 cm^{-1}; MS (30 eV), m/e (%) M$^+$ 324 (80.5), 265 (18.4), 234 (14.1), 233 (100), 218 (12.3) 206 (11.3), 205 (69.4), 179 (35.2), 178 (88.8), 165 (29.4), 156 (97.8), 155 (39.4), 128 (52.4), 127 (59.1), 59 (20.9); M_r 324.1356, found 324.1361. Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.04; H, 6.21. Found: C, 74.01; H, 6.27.

1-[3,4-(Methylenedioxy)phenyl]-5,5-dicarbomethoxy-1,3-hexadiene: yield, 102.5 mg (64.4%); pale yellow oil consisting of a mixture of two isomers in a ratio of 55:45; ^{1}H NMR ($CDCl_3$) δ 6.92–6.05 (m, 7 H), 5.92 (m, 2 H), 3.72 (s, 6 H, minor isomer), 3.71 (s, 6 H, major isomer), 1.58 (s, 3 H, minor isomer), 1.55 (s, 3 H, major isomer); ^{13}C NMR ($CDCl_3$) δ 171.2, 148.1, 147.7, 133.0, 132.7, 131.6, 131.3, 130.5, 130.4, 128.1, 127.5, 126.7, 122.8, 121.2, 109.0, 108.3, 108.1, 105.6, 100.9, 55.8, 52.5, 20.7, 20.6; IR ($CHCl_3$) 3030, 2970, 2910, 2860, 2800, 1780, 1740, 1620, 1510, 1495, 1455, 1255, 1210, 1120, 1050, 990 cm^{-1}; MS (30 eV), m/e (%) M$^+$ 318 (30.3), 259 (11.8), 227 (25.2), 199 (14.4), 172 (26.6), 150 (25.3), 140 (17.9), 121 (4.4), 107 (7.9), 59 (3.6); M_r 318.1098, found 318.1104. Anal. Calcd for $C_{17}H_{18}O_6$: C, 64.12; H, 5.70. Found: C, 64.03; H, 5.66.

1-(3-Pyridyl)-5,5-dicarbomethoxy-1,3-hexadiene: yield, 92.2 mg (67.0%); colorless oil consisting of a mixture of two diene isomers in a ratio of 53:47; ^{1}H NMR ($CDCl_3$) δ 8.62–8.43 (m, 2 H), 7.62–7.54 (m, 1 H), 7.32–7.20 (m, 1 H), 6.93–6.26 (m, 4 H), 3.76 (s, 6 H, major isomer), 3.75 (s, 6 H, minor isomer), 1.64 (s, 3 H, minor isomer), 1.58 (s, 3 H, major); ^{13}C NMR ($CDCl_3$) δ 170.6, 149.5, 148.2, 148.0, 147.8, 135.3, 134.4, 132.2, 130.9, 130.5, 129.9, 129.2, 126.7, 126.3, 123.1, 122.7, 55.9, 55.7, 52.5, 20.5; IR ($CHCl_3$) 3025, 3000, 2960, 1790, 1735, 1600, 1560, 1460, 1380, 1270, 1200, 1110, 990 cm^{-1}; MS (70 eV), m/e (%) M$^+$ 275 (31.4), 216 (57.7), 184 (23.8), 157 (22.0), 156 (100.0), 130 (33.0), 125 (15.5), 89 (11.3), 78 (13.0), 77 (17.1), 59 (30.6); M_r 275.1153, found 275.1158. Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.42; H, 6.22. Found: C, 65.44; H, 6.32.

1-(2-Furyl)-5,5-dicarbomethoxy-1,3-hexadiene: yield, 113.4 mg (85.8%); yellow oil consisting of a mixture of diene isomers A and B in a ratio of 50:50; ^{1}H NMR ($CDCl_3$) δ 7.47–7.10 (m, 2 H), 6.77–5.97 (m, 5 H), 3.73 (s, 6 H, isomer A), 3.72 (s, 6 H, isomer B), 1.64 (s, 3 H, isomer A), 1.59 (s, 3 H), isomer B); ^{13}C NMR ($CDCl_3$) δ 170.4, 153.0, 152.7, 148.5, 142.4, 141.9, 141.7, 133.0, 131.0, 130.7, 128.3, 126.6, 126.0, 120.7, 117.3, 111.2, 110.5, 56.0, 55.9, 52.6, 20.6; IR ($CHCl_3$) 3030, 2960, 1785, 1730, 1460, 1440, 1380, 1260, 1210, 1115, 1015, 990 cm^{-1}; MS (70 eV), m/e (%) M$^+$ 264 (10.0), 205 (12.2), 199 (10.1), 198 (22.2), 183 (57.1), 169 (11.9), 146 (12.3), 145 (14.9), 141 (10.3), 127 (33.6), 126 (22.7), 125 (93.3), 115 (20.3), 114 (17.2), 110 (17.1), 95 (52.7), 89 (100.0), 73 (99.8), 67 (20.5), 59 (89.8); M_r 264.0993, found 264.0998. Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.61; H, 6.10. Found: C, 63.48; H, 6.20.

1-Cyclohexyl-5,5-dicarbomethoxy-1,3-hexadiene: yield, 54.5 mg (38.9%); colorless oil consisting of a mixture of diene isomers in a ratio of 53:47. The product gives one spot by TLC, but some unidentified signals are present in the NMR spectrum. Further attempts at purification can only reduce, not eliminate the impurities present. ^{1}H NMR ($CDCl_3$) δ 6.50–5.58 (m, 4 H), 3.74 (s, 6 H, minor) 3.73 (s, 6 H, major), 2.25 (m, 1 H), 1.61 (s, 3 H, minor), 1.57 (s, 3 H, major), 1.78–0.95 (m, 10 H); IR ($CHCl_3$) 3020, 2980, 2920, 2850, 1760, 1730, 1450, 1440, 1195, 1110, 990 cm^{-1}; MS (30 eV), m/e (%) M$^+$ 280 (30.3), 279 (47.4), 221 (33.7), 220 (21.1), 199 (16.5), 198 (83.0), 190 (4.7), 189 (17.8), 183 (86.9), 161 (15.7), 146 (30.4), 135 (38.7), 134 (70.7), 125 (100.0), 95 (26.4), 89 (65.7), 83 (24.8), 59 (11.9); calcd for $C_{16}H_{24}O_4$ 280.1668, found 280.1675.

2,2-Dicarbomethoxy-3,5-undecadiene: yield, 39 mg (29.1%); colorless oil consisting of a mixture of diene isomers in a ratio of 55:45. The compound contains some unidentified impurities that cannot be eliminated by further purification. ^{1}H NMR ($CDCl_3$) δ 6.50–5.38 (m, 4 H), 3.72 (s, 6 H, major), 3.71 (s, 6 H, minor), 2.25–1.98 (m, 2 H), 1.58 (s, 3 H, minor), 1.56 (s, 3 H, major), 1.73–1.15 (m, 6 H), 0.86 (m, 3 H); IR ($CHCl_3$) 3010, 2920, 2860, 1770, 1730, 1450, 1250, 1200, 1105, 990, 840 cm^{-1}; MS (30 eV), m/e (%) M$^+$ 268 (28.8), 267 (18.9), 243 (16.9), 209 (35.6), 208 (12.5), 199 (19.1), 198 (14.1), 183 (26.4), 173 (62.9), 149 (26.6), 125 (36.5), 113 (3.5), 107 (11.9), 95 (30.4), 89 (100), 71 (5.5), 59 (25.6); calcd for $C_{15}H_{24}O_4$ 268.1668, found 268.1674.

1-Phenyl-5,5-dicarbomethoxy-1,3,8-nonatriene: yield, 120 mg (76.4%); pale yellow oil consisting of a mixture of diene isomers 1*Z*,3*E*, and 1*E*,3*E* in a ratio of 52:48; ^{1}H NMR ($CDCl_3$) δ 7.43–7.17 (m, 5 H), 6.89–6.22 (m, 4 H), 5.90–5.61 (m, 1 H), 5.10–4.90 (m, 2 H), 3.75 (s, 6 H, *E,E* isomer), 3.73 (s, 6 H, *Z,E* isomer), 2.27–1.90 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 170.2, 137.2, 136.9, 133.2, 131.9, 131.3, 130.8, 129.5, 129.0, 128.7, 128.3, 128.2, 128.0, 127.4, 126.9, 126.2, 114.8, 59.8, 59.6, 52.4, 34.9, 34.7, 28.7; IR ($CHCl_3$) 3020, 2960, 1725, 1600, 1500, 1455, 1440, 1260, 1200, 990, 920 cm^{-1}; MS (90 eV), m/e (%) M$^+$ 314 (6.2), 254 (11.9), 223 (8.7), 195 (49.8), 194 (6.9), 182 (9.4), 167 (15.0), 155 (26.6), 153 (22.3), 145 (56.1), 130 (100), 115 (33.8), 91 (70.0), 77 (18.2), 59 (35.0); M_r 314.1512, found 314.1519. Anal. Calcd for $C_{19}H_{22}O_4$: C, 72.57; H, 7.05. Found: C, 72.46; H, 7.14.

Reaction of 5 with Dimethyl Acetals Catalyzed by Trimethylsilyl Trifluoromethanesulfonate. General Procedure. A solution of 11.1 mg (10 mol%) of trimethylsilyl trifluoromethane sulfonate (TMSOTF) and 152 mg (0.5 mmol) of Bu_2SnCl_2 in anhydrous methylene chloride (1 mL) is placed in a flame-dried flask kept under nitrogen. After 15 min, 0.5 mmol of bis(silane) **5** is added in one portion at room temperature, immediately followed by the dropwise addition of 0.6 mmol of dimethyl acetal. The solution becomes immediately dark. TLC monitoring indicates the completion of the reaction. The reaction is quenched with 5 mL of saturated sodium bicarbonate solution, diluted with water (25 mL), and extracted 5 times with methylene chloride

(10 mL). the combined organic layers are dried (Na_2SO_4) and concentrated. The oil obtained is purified by preparative TLC to give an oil assigned as the *E,E* diene.

6a: yield, 60.0 mg (43.8%); pale yellow oil; ^1H NMR ($CDCl_3$) δ 7.30 (m, 5 H), 6.80 (ddd, J = 15.5, 8.3, 1.0 Hz, 1 H), 6.55 (d, J = 15.5 Hz, 1 H), 6.33 (dd, J = 15.5, 8.3 Hz, 1 H), 6.24 (broad d, J = 15.5 Hz, 1 H), 3.75 (s, 6 H), 1.62 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 171.07 s, 136.75 s, 133.28 d, 131.18 d, 130.74 d, 128.38 d, 127.94 d, 127.49 d, 126.23 d, 55.76 s, 52.78 q, 20.44 q; IR ($CHCl_3$) 3020, 2960, 1750, 1735, 1605, 1500, 1465, 1455, 1440, 1385, 1270, 1210, 1120, 1100, 990; M_r 274.1200, found 274.1205. Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.04; H, 6.61. Found: C, 69.04; H, 6.69.

6b: yield, 44.5 mg (27.4%); yellow oil; contains 5% of *Z,E* isomer; ^1H NMR ($CDCl_3$) δ 8.16–8.07 (m, 1 H), 7.90–7.38 (m, 6 H), 7.4 (d, J = 15 Hz, 1 H), 6.90 (dd, J = 15, 10 Hz, 1 H), 6.48 (dd, J = 15.5, 10 Hz, 1 H), 6.29 (d, J = 15.5 Hz, 1 H), 3.78 (s, 6 H), 1.68 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 171.0, 134.3, 133.7, 133.4, 131.5, 131.4, 130.9, 130.1, 128.4, 127.9, 125.8, 125.6, 125.3, 125.15, 56.6, 52.7, 20.8; calcd for $C_{20}H_{20}O_4$ 324.1356, found 324.1362.

7. The reaction was run on a 0.15-mmol scale, 18 mg (38.2%). The compound is only one spot by TLC, but contains impurities visible by NMR: ^1H NMR ($CDCl_3$) δ 7.44–7.08 (m, 5 H), 6.89–6.74 (m, 1 H), 6.55 (d, J = 15.8 Hz, 1 H), 6.39–6.25 (m, 2 H), 5.91–5.40 (m, 1 H), 5.19–4.81 (m, 2 H), 3.75 (s, 6 H), 2.25–1.85 (m, 4 H); calcd for $C_{19}H_{22}O_4$ 314.1512, found 314.1508.

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2,3,3-Trifluoro-1-cyclobutene and Dimers of 1,1,2-Trifluoro-1,3-butadiene from Tetrafluoroethylene–Vinylsilane Cycloadducts

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(Tetrafluorocyclobutyl)silanes prepared by thermal cycloaddition of tetrafluoroethylene (TFE) to vinylsilanes were pyrolyzed at 600 °C to give mixtures containing dimers of 1,1,2-trifluoro-1,3-butadiene. The monomeric diene **1** was undoubtedly an intermediate formed by ring opening of initially formed 2,3,3-trifluoro-1-cyclobutene (**9**). This cyclobutene has been prepared by fluoride ion catalyzed removal of trimethylfluorosilane from (2,2,3,3-tetrafluorocyclobutyl)trimethylsilane (**8**) at room temperature. One of the dimers of the diene was saturated and was shown by X-ray crystallography to have the tricyclo[3.3.0.0]octane structure (**3**) corresponding to a previously reported structure for a perfluorobutadiene dimer. The cyclooctadiene **2** presumed to be the precursor to dimer **3** and Diels–Alder dimers (vinylcyclohexenes) **4** and **7** were characterized by ^{19}F NMR analyses of liquid fractions.

Perfluorobutadiene, its dimers, and its relation to isomeric perfluorocyclobutene were first explored by W. T. Miller and co-workers.[2] A saturated dimer of the diene which they isolated was found by I. L. Karle and co-workers[3] to have the tricyclo[3.3.0.0]octane structure with two five-membered and one four-membered ring instead of the initially postulated three four-membered rings. We have now found a convenient, high-yield route to 2,3,3-trifluorocyclobutene (**9**) and have prepared dimers of 1,1,2-trifluoro-1,3-butadiene in low yield by pyrolysis of cyclobutanes prepared by cycloaddition of TFE to vinylsilanes. One of the dimers was saturated and was shown by X-ray crystallography to have structure **3** analogous to the perfluorobutadiene dimer characterized by Karle and co-workers. Other Diels-Alder dimers (vinylcyclohexenes) were characterized by ^{19}F NMR.

Results and Discussion

Five (tetrafluorocyclobutyl)silanes were prepared in high yield by cycloaddition of the corresponding vinylsilanes to TFE in sealed tubes at 180 °C (Table I). Three of these (expt 1, 2, and 3) were prepared earlier by Russian workers[4] by passing the same reactants through a quartz tube at atmospheric pressure and elevated temperatures (400–500 °C). Their yields were lower and decreased further at 600 °C. We have found that passing the cycloadducts through a quartz tube at 600 °C gives much decomposition and low yields of mixtures containing dimers of 1,1,2-trifluoro-1,3-butadiene (**1**). One of these dimers proved to be saturated and crystalline and was characterized by X-ray crystallography as having the tricyclo[3.3.0.0]octane structure **3**. Presumably pyrolysis of the (tetrafluorocyclobutyl)silanes proceeded partly through loss of fluorosilane to give 2,3,3-trifluoro-1-cyclobutene (**9**) as an intermediate which may ring open to the diene. The diene can dimerize in several ways (Scheme I). Examination of distilled fractions by NMR has provided evidence for the presence of the cyclooctadiene **2**, saturated dimer **3**, and the vinylcyclohexenes **4** and **7** with a trace of **5** (see below for structure identification).

Preparation of the presumed pyrolysis intermediate, 2,3,3-trifluoro-1-cyclobutene (**9**) has been accomplished by Park and co-workers in 21% yield by dehydrochlorination[5] and in 70% yield (63% conversion) by dechlorination[6] of the corresponding chlorofluorocyclobutanes. We have found that (2,2,3,3-tetrafluorocyclobutyl)trimethylsilane (**8**) (Table I, expt 3) in the presence of fluoride ion catalyst, loses trimethylfluorosilane to give the cyclobutene **9** in nearly quantitative yield at room temperature. As reported,[5] a white polymer separates from the uninhibited cyclobutene on standing.

Structure Identification of Dimers. Three fractions of the dimer mixture were analyzed: (A) bp 92 °C (100

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