A General Allylation Procedure Using Trimethylallylsilane and Fluoride Catalysis[1]

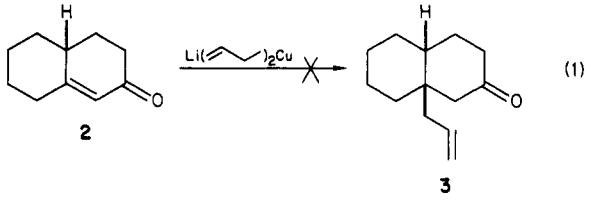
George Majetich,* Ada Casares, David Chapman, and Mark Behnke

Department of Chemistry, The School of Chemical Sciences, University of Georgia, Athens, Georgia 30602

Received September 12, 1985

The relative effectiveness for conjugate addition of lithium diallylcuprate, Lewis acid catalyzed addition of trimethylallylsilane, and fluoride ion catalyzed addition of trimethylallylsilane was compared by using a variety of Michael acceptors of differing electrophilicity and steric bulk. This study demonstrated that conjugate allylation using trimethylallylsilane and fluoride catalysis is far more general than traditional procedures and clearly superior for allylation of α,β-unsaturated esters and nitriles. This method also afforded exclusively the 1,4-adduct in allylation reactions with polyene esters and nitriles, in contrast to cuprates, which preferred 1,6-conjugate addition. The Hosomi–Sakurai allylation procedure (Lewis acid catalyzed addition of trimethylallylsilane) was effective only for conjugated enones or double activated Michael acceptors. As expected, allylations using lithium diallylcuprate were severely substrate dependent.

Conjugate addition of most nucleophilic reagents to an α,β-unsaturated carbonyl compound is achieved routinely by using an organocopper reagent or a copper-catalyzed Grignard reaction.[2] In 1969, however, House and Fischer[3] observed that the addition of lithium diallylcuprate to an α,β-unsaturated enone is highly substrate-dependent; for example, 2-cyclohexen-1-one reacts to give 3-allylcyclohexanone in 90% yield, whereas isophorone **1** gave only the tertiary alcohol via 1,2-addition. Similarly, $\Delta^{1,9}$-2-octalone **2** failed to undergo conjugate addition with lithium diallylcuprate. Ketones **1** and **2**, however, react with

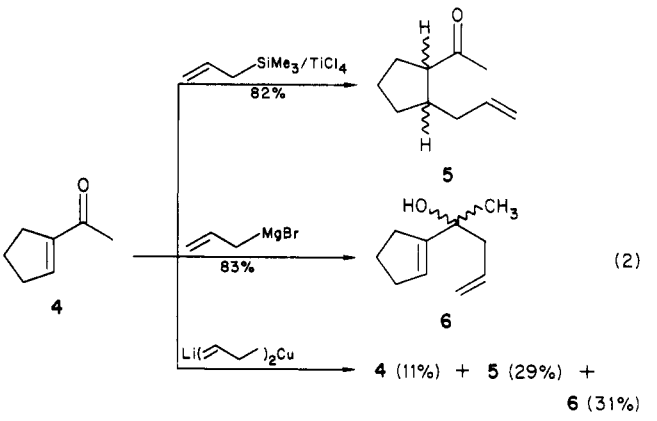


2 3 (1)

lithium dimethylcuprate or methylmagnesium bromide and a copper(I) salt to give good yields of the corresponding conjugate addition product.[3,4] These observations illustrated the need for alternative methods to allylate α,β-unsaturated systems.

Numerous organosilicon reagents for the formation of carbon–carbon bonds have been developed during the past 2 decades.[5] Calas et al.[6] were the first to demonstrate that allylsilanes add to activated carbonyl compounds such as chloroacetone in the presence of Lewis acids. Soon afterwards, Hosomi and Sakurai, reported that many carbonyl compounds react with allylsilanes, provided that the carbonyl function is activated with titanium tetrachloride.[7] They also reported that allylsilanes undergo regiospecific conjugate addition to an α,β-unsaturated enone when activated by strong Lewis acid catalysts.[8] Hosomi and Sakurai also reported the first stereoselective introduction of an angular allyl group into a fused α,β-enone by using this procedure (i.e., **2** → **3**).[8]

House and co-workers verified the superior conjugate allylation capabilities of the trimethylallylsilane/$TiCl_4$ procedure, as compared with allylmagnesium bromide/copper(I) salts and lithium diallylcuprate. Enone **4** gave a good yield of 1,4-addition product with the allylsilane-/$TiCl_4$ procedure, solely 1,2-addition with the copper-catalyzed Grignard reaction and a mixture of products with the cuprate reagent.[9]



(2)

In 1978 Hosomi and Sakurai[10] reported that the allylsilicon bond of trimethylallylsilane readily cleaves with tetra-*n*-butylammonium fluoride to generate an allylic nucleophilic species, which adds to carbonyl compounds to produce homoallylic alcohols.[11,12] However, when the electrophile is an α,β-unsaturated ketone, both conjugate addition and 1,2-addition take place competitively; e.g., treatment of (*E*)-4-phenyl-3-buten-2-one (**7**) with trimethylallylsilane and TBAF in refluxing tetrahydrofuran gives the 1,4- and 1,2-addition products (**7a** and **7b**) in 24% and 50% yields, respectively.[13] They also observed that

(1) Reported in part in a preliminary communication: Majetich, G.; Casares, A.; Chapman, D.; Behnke, M. L. *Tetrahedron Lett.* **1983**, *24*, 1909. This work was presented at the Sixth Gulf Coast Conference in Pensacola, FL, Sept 1983.

(2) Posner, G. H. *Org. React. (N.Y.)* **1972**, *19*, 1.

(3) House, H. O.; Fischer, W. F. *J. Org. Chem.* **1969**, *34*, 3615.

(4) (a) House, H. O.; Respess, W. L.; Whitesides, G. M. *J. Org. Chem.* **1966**, *31*, 3128. (b) House, H. O.; Fischer, W. F. *Ibid.* **1968**, *33*, 949.

(5) General reviews: (a) Hudrlik, P. F. "New Applications of Organometallic Reagents in Organic Synthesis"; Seyferth, D., Ed., Elsevier: Amsterdam, **1976**; p 127. (b) Colvin, E. W. *Chem. Soc. Rev.* **1978**, *78* 15. (c) Fleming, I. "Comprehensive Organic Chemistry"; Volume 3, Barton, D. H., Ollis, W. D., Eds.; Pergamon Press: Oxford, **1979**; p 541. (d) Fleming, I. *Chem. Soc. Rev.* **1981**, *10*, 83.

(6) (a) Calas, R.; Dunogues, J.; Deleris, G.; Psiciotti, F. *J. Organomet. Chem.* **1974**, *69*, C15. (b) Deleris, G.; Dunogues, J. D.; Calas, R. *Ibid.* **1975**, *93*, 43.

(7) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1296.

(8) Hosomi, A.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 1673.

(9) House, H. O.; Sayer, T. S. B.; Yau, C. C. *J. Org. Chem.* **1978**, *43*, 2153.

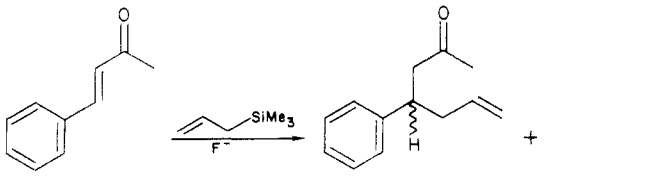
(10) Hosomi, A.; Shirhata, A.; Sakurai, H. *Tetrahedron Lett.* **1978**, 3043.

(11) For further examples of the fluoride ion induced intermolecular reaction or organosilanes with aldehydes see: Ricci, A.; Degl'Innocent, A.; Fiorenze, M.; Taddei, M.; Spartera, M. A.; Walton, D. R. M. *Tetrahedron Lett.* **1982**, *23*, 577.

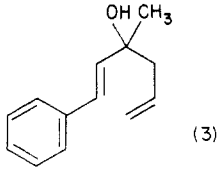
(12) For an example of the intramolecular fluoride-catalyzed addition of allylsilanes to ketones, see: (a) Ochia, M.; Sumi, K.; Fujita, E.; Shiro, M. *Tetrahedron Lett.* **1982**, *23*, 5419. (b) Trost, B. M.; Curran, D. P. *J. Am. Chem. Soc.* **1981**, *103*, 7380. (c) Trost, B. M.; Vincent, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 5680.

0022-3263/86/1951-1745$01.50/0

nitriles, epoxides, and esters fail to react with the nucleophilic species generated.[10]



7 7a



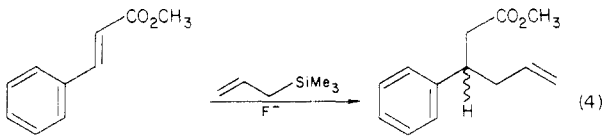
(3)

7b

Further investigation of the fluoride-catalyzed allylation with trimethylallylsilane appeared to be worthwhile. We undertook a study of α,β-unsaturated compounds of differing electrophilicity and steric bulk to determine which of these substrates preferentially undergo 1,4-addition rather than 1,2-addition during fluoride-initiated allylation. We also carried out the corresponding reactions using organocuprate and Hosomi–Sakurai allylation procedures[14] and report these findings along with those from the allylsilane/TBAF procedure.

Results and Discussion

We first investigated whether the allylic nucleophile generated by fluoride ion from trimethylallylsilane exhibits high selectivity for conjugate addition with less electrophilic Michael acceptors. To test this hypothesis, we examined methyl cinnamate (8), a substance devoid of en-



(4)

8 8a

olizable protons. Treatment of 8 with a catalytic amount[15] of TBAF in refluxing THF together with a stoichiometric quantity of trimethylallylsilane produced a 23% yield of the allylated adduct **8a**, uncontaminated with unreacted starting material.[16]

Optimization of the Conditions for Conjugate Addition. The nature of the solvent influenced the result. Dimethyl sulfoxide, diethyl ether, acetonitrile, hexane, glyme, and toluene were ineffective solvents; neat ractions were also unsatisfactory. Several investigators have observed that the presence of hexamethylphosphoramide (HMPA) in organocuprate reactions greatly influences the degree of conjugate addition.[17] We examined various THF/HMPA mixtures as the solvent system and observed conjugate addition, albeit in unacceptable yields. However, the use of dimethylformamide (DMF) gave good yields of conjugate addition. Addition of HMPA to the system improved yields further, and we chose DMF as the preferred solvent with 3 equiv of HMPA (relative to the Michael acceptor) added to the reaction. Stirring at room temperature for 15 min was sufficient to ensure complete reaction under these conditions.

Tetra-*n*-butylammonium fluoride (TBAF) proved to be the best source of fluoride ion, in either catalytic or stoichiometric amounts. Other fluoride salts such as benzyltrimethylammonium fluoride (BTAF) catalyzed the reaction sluggishly, while the alkali fluorides (KF or NaF with 18-crown-6) failed to promote any reaction. The use of cesium fluoride to initiate these reactions was not examined.[13] Although tetraalkylammonium fluorides are hygroscopic, Kuwajima and Nakamura[18] showed that they can be made essentially "anhydrous" without noticable decomposition. We developed simpler conditions for "drying" TBAF and describe them in the Experimental Section.[19]

I. Comparative Allylation Studies of α,β-Unsaturated Esters, Nitriles, and Amides

Our optimum conditions for the fluoride-induced allylation were applied to some simple Michael acceptors (Table I) and to substrates possessing enolizable protons (Table II). These tables also contain data for the $TiCl_4$-catalyzed process[20] and the organocuprate additions[21] for comparison.

A. Allylations via the Hosomi–Sakurai Reaction. Of the three methods studied, the Lewis acid catalyzed procedure was found to be the least general. The results in Tables I and II indicate that the $TiCl_4$-catalyzed allylations are heavily influenced by the electrophilic nature of the unsaturated substrate. In our hands, this allylation procedure fails with all monoactivated α,β-unsaturated esters, nitriles, or amides regardless of the choice of catalyst ($TiCl_4$, $SnCl_2$, or $BF_3{\cdot}Et_2O$). In contrast, doubly activated Michael acceptors react under $TiCl_4$-catalyzed conditions to give the conjugate addition adducts in good yield. Clearly the additional electron-withdrawing group enhances the electrophilicity of the substrate and encourages conjugate addition. Thus monoactivated α,β-unsaturated esters, nitriles, and amides are not sufficiently electrophilic to promote conjugate addition under these conditions, whereas double activated Michael acceptors (and α,β-

(13) Prior to our efforts in this area, allylation of substrate 7 represented the sole literature example. While our initial manuscript was in press,[1] an example of the allylation of cyclohexenone using cesium fluoride as catalyst was reported: Ricci, A.; Fiorenza, M.; Grifagni, M. A.; Bartolinie, G. *Tetrahedron Lett.* **1982**, *23*, 5079.

(14) For comprehensive reviews of allylsilanes in organic synthesis, see: (a) Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1. (b) Hosomi, A.; Sakurai, H. *J. Syn. Org. Chem. Jpn.* **1985**, *43*, 406.

(15) 0.05 → 0.2 molar equiv of the fluoride ion (relative to the Michael acceptor) were routinely employed.

(16) For a comprehensive review of the use of the $CSi(CH_3)_3$ moiety as a protected carbanion, see: Andersen, N. H.; McCrae, D. A.; Grotjahn, D. B.; Gabhe, S. Y.; Theodore, L. J.; Ippolito, R. M.; Sarkar, T. K. *Tetrahedron* **1981**, *37*, 4079.

(17) (a) House, H. O.; Lee, T. U. *J. Org. Chem.* **1978**, *43*, 4369. (b) El-Bour, M.; Wartski, L *Tetrahedron Lett.* **1980**, *21*, 2897. (c) Ziegler, F. E.; Tam, C. C. *Ibid.* **1979**, 4717.

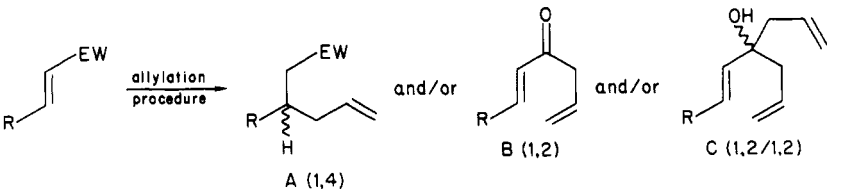
(18) (a) Kuwajima, I.; Nakamura, E.; Shimizu, M. *J. Am. Chem. Soc.* **1982**, *104*, 1025. (b) Noyori, R.; Yokoyama, K.; Sakata, J.; Kuwajima, I.; Nakamura, E.; Shimizu, M. *J. Am. Chem. Soc.* **1977**, *99*, 1265.

(19) A recent paper [Cox, D. P.; Terpinski, J.; Lawrynowicz, W. *J. Org. Chem.* **1984**, *49*, 3216] reported similar observations in the preparation of "anhydrous" tetra-*n*-butylammonium fluoride.

(20) The procedure reported by Sakurai and Hosomi[8] was used to perform the Lewis acid catalyzed allylations. If, after stirring at room temperature for several hours (>12 h), thin layer chromatography indicated that no reaction had taken place, the reaction mixture was recooled to −78 °C and a solution of (*E*)-4-phenyl-3-buten-2-one [7, a compound shown to undergo 1,4-addition in high yield] in CH_2Cl_2 was added. Subsequent quenching and purification of the reaction resulted in the isolation of the 1,4-adduct **7a** and unreacted initial substrate. These results indicate that although the reagents were still viable, the initial substrate had failed to undergo allylation. On several occasions, boron trifluoride etherate was used as the catalyst. The experimental conditions of Andersen and co-workers were employed: Sarkar, T. K.; Andersen, N. H. *Tetrahedron Lett.* **1970**, 3513.

(21) Conjugate addition of lithium diallylcuprate was carried out by using a modification of the procedure of Whitesides and co-workers.[22,23] Solutions of the cuprate reagent were tested by reaction with cyclohexenone; the corresponding 1,4-adduct was produced in 95% yield, which is consistent with published results.[3] We found that 1.5 equiv of the organocuprate gave optimum results.

Table I



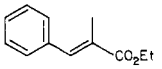
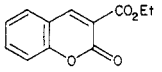
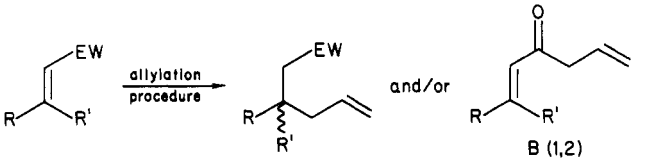
R	EW	F^-/ SiMe$_3$ %A	%B	%C	$TiCl_4$/ SiMe$_3$ %A	%B	%C	Li( )$_2$Cu %A	%B	%C
	CO_2CH_3 (8)	90	0	0	no reaction			61	9	0
	CN (9)	65	0	0	no reaction			52	0	0
	$CONEt_2$ (10)	80	0	0	no reaction			decomposes		
	CO_2Et (11)	83	0	0	no reaction			70	10	6
	CN (12)	91	0	0	no reaction			73	0	0
	$CONEt_2$ (13)	84	0	0	no reaction			33	0	0
	CO_2Et (14)	80	0	0	no reaction			0	39	39
	CN (15)	65	0	0	no reaction			46	0	0
	$CONEt_2$ (16)	0	0	27	no reaction			0	40	16
H	$CO_2CH_2C_6H_5$ (17)	65	0	0	no reaction			28	0	0
CO_2CH_3	CO_2CH_3 (18)	80	0	0	no reaction			64	0	0
 19		80	0	0	no reaction			0	39	9
 20		91	0	0	49	0	0	83	0	0

Table II



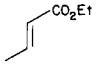
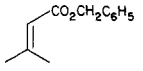
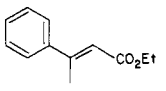
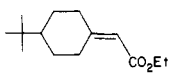
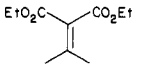
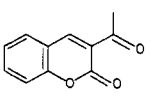
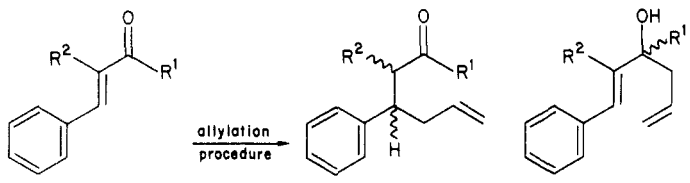
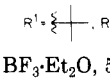
	F^-/ SiMe$_3$ %A	%B	$TiCl_4$/ SiMe$_3$ %A	%B	Li( )$_2$Cu %A	%B
 21	27	0	no reaction		0	31
 22	deprotonation		no reaction		27	0
 23	47	0	no reaction		0	64
 24	deprotonation		no reaction		0	31
 25	52	0	35	0	86	0
 26, X = $CO_2CH_2C_6H_5$ 27, X = CN	50 44	0 0	no reaction no reaction		15 23	25 0
 28	22	0	79	0	decomposed	

Table III



A (1,4) B (1,2)

	F^-/ SiMe$_3$		$TiCl_4$/ SiMe$_3$		Li( )$_2$Cu	
	%A	%B	%A	%B	%A	%B
R^1 = H; R^2 = H (**29**)	0	86	0	0[a]	0	87
R^1 = H; R^2 = CH_3 (**30**)	0	92	0	0[b]	0	81
R^1 = CH_3; R^2 = H (**7**)	25	50	89	0	31	46
 ; R^2=H (**31**)	57	20	74	0	17	6
 , R^2=H (**32**)	58	26	92	0	45	43

[a] With BF_3·Et_2O, 50% **29b**. [b] With BF_3·Et_2O, 45% **30b**.

ethylenic ketones; see Table III) are.

B. Allylations via Cuprate Addition. As expected, organocuprate allylations were troublesome (with 1,4-, 1,2-, and/or 1,2-/1,2-condensations[24] being observed) and seemed to be influenced by both steric and electronic factors. 1,2-Addition predominated for highly substituted (less electrophilic) substrates; for example, the β,β-disubstituted esters **23** and **24** failed to give any 1,4-adducts, giving predominantly 1,2-addition products.

In general, α,β-unsaturated nitriles give good yields of 1,4-addition; doubly activated esters gave excellent yields of the conjugate addition products (in contrast to reaction with monoactivated unsaturated esters). The activating effect of the additional electron-withdrawing substitutent augments conjugate addition of organocuprates. Surprisingly, the α,β-unsaturated amide **13** reacted in conjugate fashion with $LiCu(CH_2CH{=}CH_2)_2$,[25] whereas 1,2-addition predominated with amide **16**.

C. Allylations via Fluoride Ion Catalysis. Under fluoride catalysis conditions, only 1,4-conjugate addition was observed for either α,β-unsaturated esters or nitriles. In general, this procedure was superior to the use of lithium diallylcuprate for conjugate allylation; the $TiCl_4$-catalyzed process failed completely for the substrates listed.

We found that fluoride-induced allylation is partially substrate-dependent. Although conjugate addition predominates, yields of the 1,4-adducts vary; e.g., ethyl-2-butenoate (**21**) reacted in only 27% yield, whereas the analogous fully substituted ester (**14**) yielded 80% of the 1,4-adduct. The major side reaction was not proton abstraction (because of the allylic nucleophilic species generated), but the secondary condensation of the initially allylated material with unreacted substrate. High dilution of the reagents failed to suppress this competing process. Evidently proton abstraction by the allylic nucleophile becomes a major concern only for severely hindered β,β-disubstituted Michael acceptors. Not all of the β,β-disubstituted substrates examined were plagued by competive deprotonation: diester **25** gave exclusively 1,4-addition (in 52% yield), despite its known ease of deprotonation with a wide variety of bases, and substrate **23** gave the 1,4-adduct in 47% yield.

II. Comparative Allylation Studies of α,β-Ethylenic Ketones and Aldehydes

We also examined the effectiveness of the three allylation procedures with α,β-unsaturated ketones and aldehydes (Table III).

A. Allylation of α,β-Unsaturated Aldehydes. Not surprisingly, cinnamaldehyde (**29**) and α-methylcinnamaldehyde (**30**) failed to undergo conjugate addition with any of the three allyl species. For example, **30**, which undergoes conjugate addition with lithium dimethylcuprate,[2] gave only the 1,2-adduct with either lithium diallylcuprate or the F^-/trimethylsilane procedure. This is undoubtably due to the well-established tendency of enals to undergo 1,2-addition with most organometallic reagents.[26] Note, however, that **29** and **30** failed to react with $TiCl_4$/trimethylallylsilane; Hosomi and Sakurai had previously reported that β,δ-unsaturated alcohols are readily formed by the action of these reagents on aldehydes.[7] We believe that the highly reactive enal functionality is rapidly consumed by a $TiCl_4$-catalyzed 1,2-addition of chloride ion, producing a hemichloroacetal which is hydrolyzed back to the aldehyde upon aqueous workup. To test this we duplicated several reported 1,2-allylations with aliphatic aldehydes using either $TiCl_4$ or BF_3·Et_2O as the catalyst.[7] However, when enals **29** and **30** were examined, only those reactions catalyzed by BF_3·Et_2O produced a product (1,2-addition, 50% yield). These observations support our hypothesis concerning the $TiCl_4$-catalyzed 1,2-addition of chloride to enals.

B. Allylations of α,β-Unsaturated Ketones. Conjugate addition of the allyl group to enones occurred in high yields by using the Sakurai procedure, whereas the fluoride-induced allylation and cuprate procedures gave mixtures of 1,2- and 1,4-addition products: yields of the 1,4-adduct varied depending on the steric environment of

(22) Whitesides, G. M.; Fischer, W. F.; Filippo, J. S.; Bashe, R. W. *J. Am. Chem. Soc.* **1969**, *91*, 4871.

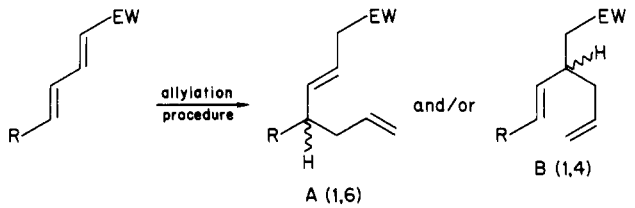
(23) In our hands, the generation of lithium diallylcuprate by the cleavage of allylphenyl ether with metallic lithium proved less satisfactory: Eisch, J. J.; Jacobs, A. M. *J. Org. Chem.* **1963**, *28*, 2145.

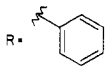
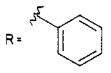
(24) The initial 1,2-adduct is an α,β-unsaturated enone capable of further 1,2-(or 1,4-) attack; due to steric influences only secondary 1,2-additions occurred to generate the corresponding tertiary allylic alcohols.

(25) Recently the tandem conjugate addition–α-alkylation of α,β-unsaturated amides has attracted considerable interest: (a) Mpango, G. B.; Mahalanabis, K. K.; Mahdavi-Damghani, Z.; Snieckus, V. *Tetrahedron Lett.* **1980**, *21*, 4823 and references cited therein. (b) Baldwin, J. E.; Dupont, W. A. *Tetrahedron Lett.* **1980**, *21*, 1881 and references cited therein.

(26) Eicher, T. "The Chemistry of Carbonyl Compounds"; Patai, S.; Ed.; Interscience Publishers: New York, 1966; pp 624–631 and 662–678. Recently organozinc reagents have been shown to undergo conjugate addition to enals in good yields: de Souza Barboza, J. C.; Petrier, C.; Luche, J. L. *Tetrahedron Lett.* **1985**, *26*, 829.

Table IV



	F^-/ SiMe$_3$		$TiCl_4$/ SiMe$_3$		Li( )$_2$Cu	
	%A	%B	%A	%B	%A	%B
EW = CN (33) 	0	37	no reaction		80	0
EW = CO_2Et (34) 	0	63	no reaction		95	0
EW = CO_2Et (35) R = CH_3	0	31	no reaction		61	0

the carbonyl moiety.[27] For example, (*E*)-4-phenyl-3-buten-2-one (**7**) led to predominantly 1,2-adducts, in contrast to 2,2-dimethyl-5-phenyl-4-penten-3-one (**32**), which gave largely 1,4-adducts with both allylation procedures.

III. Regioselectivity in Allylations of Diene Esters and Nitriles

The substrates studied so far have had the potential for either 1,2- or 1,4-addition. We also studied polyene esters and nitriles which have an additional option, 1,6-conjugate addition (Table IV). Munch-Peterson and co-workers showed that in similar examples, copper-catalyzed Grignard reagents react at the terminal carbon atom of the conjugated system.[28] Marshall et al. reported that 1,4-conjugate addition of organocuprate reagents is favored when the competing electrophilic centers are in roughly equivalent steric environments.[29]

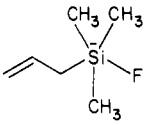
Treatment of substrates **33**, **34**, and **35** with lithium diallylcuprate produced the 1,6-adducts exclusively, all in good yield; these results are consistent with Daviaud and Miginac's observation that *sec*-butyl sorbate undergoes only 1,6-addition with lithium diallylcuprate.[30] *Remarkably, the fluoride-induced allylation procedure provided the 1,4-addition product exclusively though in modest yields.*[31] As yet, we have not established which factors govern this selectivity. However, this reactivity for 1,4-addition has been exploited within the intramolecular context.[32]

IV. Mechanistic Considerations

Three species participate in the fluoride induced allylation reaction: TBAF, trimethylallylsilane, and the Michael acceptor. Since a trimolecular reaction is unlikely to occur, a reactive intermediate which results from the interaction of two of the three components is more plausible. In their original report of the fluoride ion-induced allylation, Hosomi and Sakurai suggested that a free allyl anion was the reactive intermediate,[10] due to the substantial difference in the Si–C and Si–F bond strengths, the counter cation being a tetra-*n*-butylammonium ion. In 1980 DePuy reported that, in the gas phase, reaction of fluoride ion with allyltrimethylsilane rapidly produces the allyl anion.[33]

In solution, however, the high pK_a of propene, the conjugate acid of an allylic carbanion makes the intermediacy of an allylic anion in this allylation procedure quite unlikely. We believe that the ambident nucleophilic species involved is a nonbasic hypervalent silicon intermediate resulting from fluoride ion addition to silicon. Such

Hosomi-Sakurai postulated reactive intermediate



(5)

pentacoordinate organosilicon intermediate

(27) It is well-established that steric bulk adjacent to the carbonyl moiety enhances conjugate addition for α,β-unsaturated enones with various nucleophiles. For example, see: (a) Hunig, S.; Wehner, G. *Chem. Ber.* **1980**, *113*, 302; **1980**, *113*, 324. Seuron, N.; Wartski, L.; Seyden-Penne, J. *Tetrahedron Lett.* **1977**, 4557. (c) Stork, G.; Maldonado, L. *J. Am. Chem. Soc.* **1974**, *96*, 5272. (d) Hunig, S.; Oller, M. *Chem. Ber.* **1980**, *113*, 3803.

(28) Munch-Petersen, J. *Bull. Soc. Chim. Fr.* **1966**, 471. (b) Bretting, C.; Munch-Petersen, J.; Jorgensen, P. M.; Refin, S. *Acta Chem. Scand.* **1960**, *14*, 151. (c) Munch-Petersen, J.; Bretting, C.; Jorgensen, P. M.; Refin, S.; Andersen, I. G. K. *Ibid.* **1961**, *15*, 277. (d) Jacobsen, S.; Jart, A.; Kindt-Larsen, T.; Andersen, I. G. K.; Munch-Petersen, J. *Ibid.* **1963**, *17*, 2423.

(29) Marshall, J. A.; Ruben, R. A.; Hirsch, L. K.; Phillippe, M. *Tetrahedron Lett.* **1971**, 3795.

(30) Daviaud, G.; Miginiac, P. *Tetrahedron Lett.* **1973**, 3348.

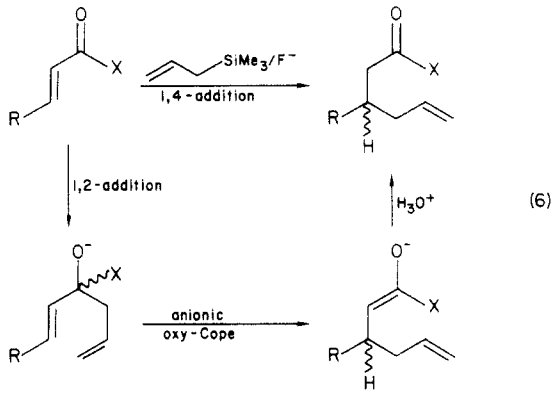
(31) We Examined the Cope rearrangements of substrates **34a** (the 1,6-adduct) and **34b** (1,4-adduct). Pure adduct **34a** was heated at 190 °C in a sealed tube for 16 h. Analysis of the resulting mixture revealed the presence of both **34a** and **34b**, indicating that some rearrangement had taken place; longer reaction times (or higher reaction temperatures) failed to change this equilibrium mixture and resulted in decomposition. In contrast, adduct **34b** (obtained from the fluoride induced allylation) failed to undergo rearrangement despite numerous attempts. These results suggest that adduct **34b** is slightly more thermodynamically stable, owing to conjugation of the disubstituted olefin with the phenyl substitutent.

(32) The intramolecular addition of allylsilanes to conjugated dienones has been shown to permit the facile entry into a wide variety of bicyclic ring systems via either intramolecular 1,4- or 1,6-addition: (a) Majetich, G.; Hull, K.; Defauw, J.; Shawe, T. *Tetrahedron Lett.* **1985**, *26*, 2755. (b) Majetich, G.; Hull, K.; Desmond, R. *Tetrahedron Lett.* **1985**, *26*, 2751. (c) Majetich, G.; Hull, K.; Defauw, J.; Desmond, R. *Tetrahedron Lett.* **1985**, *26*, 2747. (d) Majetich, G.; Behnke, M.; Hull, K. *J. Org. Chem.* **1985**, *50*, 3615.

(33) DePuy, C. H.; Bierbaum, M. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5012.

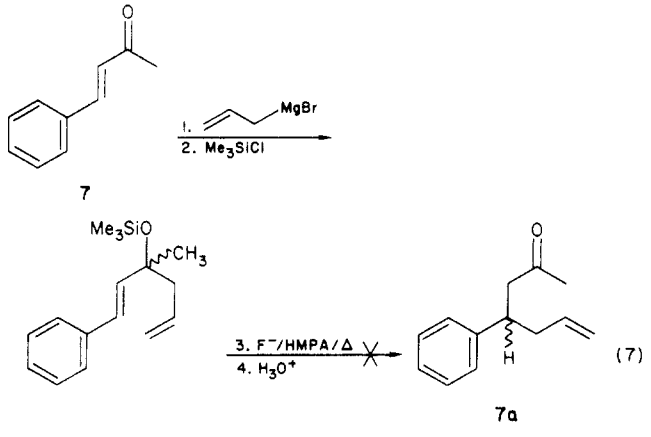
pentacoordinate silicon intermediates have been isolated[34] and implicated as reactive intermediates in several cases.[35] Although a nonbasic pentacoordinate organosilicon intermediate accounts for the remarkable selectivity demonstrated by this allylation procedure, the actual nature of the nucleophilic species has not yet been determined.

Our results show that the nucleophile generated by treatment of allyltrimethylsilane with a fluoride salt reacts predominantly in conjugate fashion, a propensity of stabilized nucleophiles with Michael acceptors. However, an alternative mechanism involving 1,2-addition, followed by an anionic oxy-Cope rearrangement,[36] would produce the same products as conjugate addition.



(6)

In an attempt to address this issue, we prepared the trimethylsilyl ether of tertiary alcohol **7b** and treated it with fluoride ion. In our hands, employing a variety of thermolysis conditions [the harshest being thermolysis in a sealed tube at 110 °C for 14 h using a twofold excess of fluoride ion with HMPA as solvent], the oxy-Cope rearrangement product **7a** was not obtained. In contrast, fluoride induced allylation proceeded rapidly at room temperature. Because of these preliminary results, the 1,2-addition/anionic oxy-Cope rearrangement mechanism was deemed unlikely.



(7)

We were unable to detect a silyl ketene acetal intermediate in the fluoride-induced reactions of unsaturated esters or amides; the analagous silylated enamines were also not observed during the allylation of α,β-unsaturated nitriles. On occasion, the silyl enol ethers or the silyl ethers of the 1,2-adducts were obtained from the fluoride-induced allylation of α,β-unsaturated ketones; methanolysis of the reaction mixture effectively hydrolyzed these intermediates.

Conclusion

Of the three methods compared in this paper, conjugate addition of the allyl moiety using trimethylallylsilane and tetra-*n*-butylammonium fluoride proved far more general than the two alternative methods. The fluoride ion catalyzed procedure is clearly superior for α,β-unsaturated esters and nitriles. When applied to α,β-ethylenic ketones, however, these conditions gave mixtures of 1,2- and 1,4-addition products. $TiCl_4$ and trimethylallylsilane (the Hosomi–Sakurai reaction) give the best yields with these ketones. Organocopper allylations are highly substrate-dependent. Furthermore, allylsilanes undergo exclusive 1,4-conjugate addition with polyene esters and nitriles, rather than 1,6-addition. Fluoride-induced allylation appears to be an attractive method for conjugate addition to a wide variety of Michael acceptors under mild conditions.

Experimental Section

Infrared spectra (IR) were recorded on a Perkin-Elmer 297 infrared spectrophotometer. Nuclear magnetic resonance spectra (NMR) were recorded on a Varian EM-390 spectrophotometer, using tetramethylsilane as the internal standard at 0.00 ppm. Low-resolution mass spectra (MS) were recorded on a Finnigan 4023 gas chromatograph/mass spectrometer, by a direct probe and are expressed in m/z units. Microanalysis was performed by Atlantic Microlab, Inc., Atlanta, GA.

Anhydrous tetrahydrofuran (THF) and diethyl ether were purified by refluxing with, and distillation from, sodium benzophenone ketyl under a nitrogen atmosphere. Anhydrous dimethylformamide (DMF) and hexamethylphosphoramide (HMPA) were purified by refluxing over and distillation from calcium hydride under a dry nitrogen atmosphere. All reactions were performed under an inert atmosphere of dry nitrogen.

Materials. Registry numbers are provided for known compounds not commercially available.[37-40] Spectral data for new compounds such as **16** and **31** are provided below.

Table I.[37] Methyl cinnamate (**8**), diethyl fumarate (**18**), and 2-(ethoxycarbonyl)coumarin (**20**) were purchased from Aldrich. α,β-Unsaturated esters **11** and **14** were prepared by the condensation of the anion of triethyl phosphonoacetate (i) with 3-furfural (92%) and trimethylacetaldehyde (98%). α,β-Unsaturated nitriles **9**, **12**, and **15** were prepared by using the Wadsworth–Emmons condensation of the anion derived from diethyl (cyanomethyl)-phosphonate (ii) with benzaldehyde (74%), 3-furfural (48%), and trimethylacetaldehyde (41%). Addition of the anion of diethyl [(*N*,*N*-diethylcarbamoyl)methyl]phosphonate[42] to benzaldehyde, 3-furfural, and trimethylacetaldehyde produced α,β-unsaturated amides **10**, (81%), **13** (61%), and **16** (62%). Wittig condensation of benzaldehyde with carbomethoxymethylenetriphenylphosphorane gave substrate **19** in 87% yield.

Table II.[38] 2-Acetylcourmarin (**28**) and ethyl crotonate (**21**) were commercially available from Aldrich. Diethylisopropylidiene

(34) The pentafluorosilicate ion is found in salts such as $[Ph_4As]^+[SiF_5]^-$. Data for SiF_5^- ions and also for similar species $RSiF_4^-$ and $R_2SiF_3^-$ are also known. For examples of penta- or hexacoordinate silicon species, see: (a) Schomburg, D.; Frebs, R. *Inorg. Chem.* **1984**, *23*, 1378. (b) Voronkow, M. G.; Deriglazov, N. M.; Brodskaya, E. I.; Kalistratova, E. E.; Gubanova, L. I. *J. Fluorine Chem.* **1982**, *19*, 299. (c) Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *198*, 231. (d) Tamao, K.; Mishima, M.; Yoshida, J.; Takahashi, M.; Ishida, M.; Kumada, M. *J. Organomet. Chem.* **1982**, *225*, 151. (e) Varonkov, M. G. *Pure Appl. Chem.* **1966**, *13*, 35. (f) Turley, J. W.; Boer, F. P. *J. Am. Chem. Soc.* **1968**, *90*, 4026.

(35) For a comprehensive review discussing hypervalent silicon species as intermediates in the reactions of organosilicon compounds, see: Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. "Stereochemistry at Silicon"; in "Topics in Stereochemistry"; Eliel, E. L., Wilen, S. H., Allinger, N. L., Eds.; Wiley-Interscience: New York, 1984; Vol. XV, pp 43–198.

(36) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765.

(37) **9**, 1885-38-7; **10**, 3680-04-4; **11**, 623-20-1; **12**, 6125-63-9; **13**, 51825-02-6; **14**, 22147-62-2; **15**, 29582-19-2; **17**, 2495-35-4; **19**, 7042-33-3. Spectral data for **16**: NMR ($CDCl_3$) δ 1.25 (t, 6 H, J = 7 Hz), 3.5 (q, 4 H, J = 7 Hz), 6.4–6.7 (m, 2 H), 7.1 (AB q, 2 H, $\Delta\nu_{AB}$ = 44 Hz, J = 14 Hz), 7.5 (br s, 1 H).

(38) **22**, 37526-89-9; **23**, 945-93-7; **24**, 13733-50-1; **27**, 3047-38-9. Spectral data for **26**: NMR (CCl_4) δ 1.9–2.3 (m, 2 H), 2.3–2.9 (m, 4 H), 5.3 (s, 2 H), 6.8–7.0 (m, 1 H), 7.4 (br s, 5 H).

malonate (**25**) was prepared in 46% yield by an acid-catalyzed condensation between diethyl malonate and acetone.[43] α,β-Unsaturated esters **23** and **24** were produced by the condensation of the anion of (i) with acetophenone (82%) and 4-*tert*-butylcyclohexanone (82%). Δ^1-Cyanocyclopentene (**27**) was prepared in 45% yield by dehydration ($SOCl_2/\Delta$) of cyclopentanone cyanohydrin. Hydrolysis of **27** afforded Δ^1-cyclopentencarboxylic acid (90%) which was converted into ester **26** by treatment with thionyl chloride, followed by the addition of the lithium salt of benzyl alcohol (67% yield overall). Substrate **22** was prepared by generating its acid chloride ($SOCl_2$) and adding the lithium salt of benzyl alcohol.

Table III.[39] Cinnamaldehyde (**29**), α-methylcinnamaldehyde (**30**), and (*E*)-4-phenyl-3-buten-2-one (**7**) are commercially available from Aldrich. Benzalpinacolone (**32**) was prepared via an aldol reaction (68%).[44] 1-Phenyl-4-methyl-1-hexen-3-one (**31**) was prepared in 42% overall yield from cinnamaldehyde by addition of *sec*-butyllithium (−20 °C), followed by Jones oxidation at 0 °C.

Table IV.[40] Ethyl sorbate (**35**) is commercially available from Aldrich. A Wadsworth–Emmons condensation of cinnamaldehyde with the phosphonate anions of i and ii produced substrates **33** and **34** in 74% and 87% yield, respectively.

General Procedure for Drying Tetra-*n*-butylammonium Fluoride (TBAF). Heating commercially available TBAF (Aldrich or Alfa) neat under high vacuum at temperatures greater than 80 °C resulted in decomposition and poor allylation reactions; heating at lower temperatures (40 °C) avoided these difficulties. We found, however, that virtually anhydrous TBAF could be prepared without heating. A small amount of TBAF (usually 10 → 30 mg) was placed under high vacuum (<0.1 mmHg) for $^1/_2$ h at room temperature. The flask was then flushed with nitrogen and 2 mL of dry DMF was added. The resulting solution was transferred (via syringe) to a round-bottomed flask (under nitrogen) containing 300 mg of 4-Å molecular sieves (which had been activated by flame-drying for 5 min under high vacuum) and a micro stirring bar. The resulting mixture was allowed to stir for $^1/_2$ h prior to use and then transferred to the reaction vessel (which also contained flame-dried 4-Å molecular sieves).[45] Freshly prepared solutions of TBAF/DMF were always employed in allylations. However, stock solutions of DMF/TBAF stored at room temperature were found effective for about 1 day.

A. General Procedure for the Fluoride-Induced Allylations. All allylation reactions were carried out on 100 mg of Michael acceptor; scaling-up of the reaction (up to 500 mg of substrate) had little impact (±5%) upon the overall yield. Typically 3 equiv of trimethylallylsilane and HMPA were used relative to the quantity of Michael acceptor. On occasion, however, additional trimethylallylsilane was necessary to achieve total conversion; this additional material was added 1 equiv at a time until TLC analysis indicated that the starting material had been consumed. At no time were greater than 6 equiv (total) of trimethylallylsilane necessary to achieve complete reaction. The following experimental procedure is typical.

Methyl 3-Phenyl-5-hexenoate (8a). A reaction vessel containing 100 mg of 4-Å molecular sieves was flame-dried under vacuum (5 min) and placed under nitrogen. A solution of 20 mg of anhydrous TBAF in 2 mL DMF was then added. Methyl cinnamate (**8**) (100 mg, 0.62 mmol) dissolved in 1 mL of DMF was then added. A solution of 331 mg of HMPA (1.8 mmol) and 212 mg of freshly distilled allylsilane (1.8 mmol) in 2 mL of DMF was then added dropwise to the reaction vessel at room temperature. Coloration occurred immediately. After 10 min, TLC analysis revealed that reaction was complete. After methanolysis of the reaction mixture using 1 mL of 1 M HCl in methanol, the reaction mixture was diluted with 20 mL of water. Workup afforded 170 mg of residue which was homogenous on TLC. Column chromatography afforded 101 mg (79%) of **8a**.

B. General Procedure for the $TiCl_4$-Catalyzed Allylations. All allylation reactions were carried out by using 1 equiv of Michael acceptor, 1 equiv of titanium tetrachloride and 1.1 equiv of trimethylallylsilane; reactions were typically performed on 200 mg of substrate. Sakurai's original procedure[8] was employed successfully with substrates **20**, **25**, **30**, **7**, **31**, and **32**; however, all other substrates failed to undergo reaction. *This conclusion was experimentally demonstrated in each case by using the following procedure.*

Attempted Allylation of Methyl Cinnamate (13).[20] $TiCl_4$ was added dropwise to a solution of **8** in CH_2Cl_2 at −30 °C. The mixture was stirred for 5 min and then precooled trimethylallylsilane was slowly added. After 5 min TLC indicated no reaction, so the mixture was gradually warmed to room temperature over a 12-h period. TLC analysis again indicated no reaction so the mixture was recooled to −30 °C, and a CH_2Cl_2 solution of **7** was added. After 10 min the TLC indicated that substrate **7** had been consumed. After the reaction was quenched with water and extracted with ether, the organic phase was washed sequentially with water, brine, and saturated ammonium chloride solution. After drying with $MgSO_4$ and filtering, the solvents were evaporated in vacuo. Column chromatography afforded the 1,4-adduct **7a** in 70% yield and unreacted methyl cinnamate.

C. General Procedures for Lithium Diallylcuprate Allylations.[21] All allylation reactions were carried out by using 1 equiv of Michael acceptor and 1.5 equiv of organocuprate reagent [prepared by adding 3 equiv of *n*-BuLi to 0.75 equiv of tetraallyltin and 1.5 equiv of anhydrous copper(I) iodide]. Additional amounts of cuprate or longer reaction times at elevated temperatures gave predominantly the allylic tertiary alcohols.[24] Reactions were carried out by using 100–200-mg quantities of Michael acceptor. The following experimental procedure is typical.[22]

3-Phenyl-5-hexenenitrile (9a). *n*-Butyllithium (1.6 M, 2.13 mL, 3.4 mmol) was added to tetraallyltin (241 mg, 0.85 mmol) at 0 °C. After stirring for 5 min, the hexanes were evaporated in vacuo, whereupon ether (5 mL) was added to the residue. The resulting solution was transferred to a second reaction vessel containing cuprous iodide (325 mg, 1.7 mmol) in ether (5 mL) at 0 °C. The mixture was stirred for 15 min, and then a solution of nitrile **9** (200 mg, 1.6 mmol) in ether (2 mL) was added dropwise. The mixture was warmed to room temperature, stirred for 1 h, quenched with NH_4Cl solution, and extracted with ether, and the organic phase was washed with water and brine. The ether solution was dried with $MgSO_4$, filtered, and concentrated. Column chromatography afforded 140 mg (52%) of **9a**.

Spectral Properties of Products. The general procedures for fluoride ion catalyzed, the $TiCl_4$-catalyzed, and the lithium diallylcuprate allylations have been abbreviated as A, B, and C, respectively. For example, methyl 3-phenyl-5-hexenoate (**8a**) was prepared via the fluoride-induced allylation in 90% yield, and the lithium diallylcuprate procedure in 61% yield; no **8a** was obtained by using the $TiCl_4$-catalyzed procedure. This information appears below as methyl 3-phenyl-5-hexenoate (**8a**): A, 90%; C, 61%.[41]

4-Phenyl-7-hepten-2-one (7a):[10] A, 25%; B, 89%; C, 31%; NMR ($CDCl_3$) δ 1.87 (s, 3 H), 2.27 (t, 2 H, J = 6 Hz), 2.52 (t, 2 H, J = 6 Hz), 2.9–3.2 (m, 1 H), 4.7–5.0 (m, 2 H), 5.3–5.7 (m, 1 H), 7.0–7.1 (m, 5 H); IR (film) 2910, 1706, 738, 686 cm^{-1}; MS, m/z 188 (M^+), 147 (M − 41).

3-Methyl-1-phenyl-1,5-hexadien-3-ol (7b):[10] A, 50%; C, 46%; NMR ($CDCl_3$) δ 1.34 (s, 3 H), 1.90 (s, 1 H), 2.2–2.4 (m, 2 H), 4.8–5.2 (m, 2 H), 5.4–5.8 (m, 1 H), 6.25 (AB q, 2 H, $\Delta\nu_{AB}$ = 30 Hz, J = 15 Hz), 6.9–7.3 (m, 5 H); IR (film) 3650–3150, 3080, 3020, 2970, 2930, 1640, 1600, 1495, 1450, 1370, 1200, 975, 920, 795 cm^{-1}; MS, m/z 170 (M − 18), 147 (M − 41).

(39) **31**, 21903-53-7.

(40) **33**, 5785-22-5; **34**, 14164-31-9.

(41) In general, only spectral properties of new compounds are listed. However, in several cases the spectral data of "known" compounds are provided. In these instances, such data was not available from earlier workers for comparison.

(42) Landor, P. D.; Landor, S. R.; Odyek, O. *J. Chem. Soc., Perkin Trans. 1* **1977**, 33.

(43) Eliel, E. L.; Hutchins, R. O.; Knoeber, M. *Org. Synth.* **1970**, *50*, 38.

(44) Hill, G. A.; Bramann, G. M. *Organic Syntheses*; Gilman, H., Blatt, A. H., Eds.; Wiley: New York, 1932; Collect. Vol. I, p 81.

(45) Activated molecular sieves catalyze numerous reactions, e.g., enamine and aldol condensations. This was examined by duplicating the general procedure for the fluoride ion induced allylations without the presence of fluoride ion using methylcinnamate. After 2 days at room temperature, TLC analysis indicated no reaction. Addition of a catalytic quantity of fluoride ion resulted in exclusive formation of methyl 3-phenyl-5-hexenoate.

Methyl 3-phenyl-5-hexenoate (8a): A, 90%; C, 61%; NMR ($CDCl_3$) δ 2.1–2.5 (m, 5 H), 3.0–3.2 (m, 1 H), 3.45 (s, 3 H), 4.7–5.0 (m, 2 H), 5.25–5.8 (m, 1 H), 6.9–7.1 (m, 5 H); IR (film) 2960, 1740, 1160, 990, 905, 752, 690 cm^{-1}; MS, m/z 173 (M – 41). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.55; H, 7.92.

1-Phenyl-1,5-hexadien-3-one (8b): C, 9%; NMR ($CDCl_3$) δ 2.28 (d, 2 H, J = 6 Hz), 4.8–5.8 (m, 3 H), 6.25 (AB q, $\Delta\nu_{AB}$ = 20 Hz, J = 14 Hz), 6.9–7.2 (m, 5 H); IR (film) 3050, 3015, 2920, 1680, 1600, 1495, 1450 cm^{-1}; MS, m/z 172 (M^+).

3-Phenyl-5-hexenenitrile (9a): A, 65%; C, 52%; NMR ($CDCl_3$) δ 2.2–2.5 (m, 4 H), 2.6–3.0 (m, 1 H), 4.75–5.05 (m, 2 H), 5.2–5.75 (m, 1 H), 6.8–7.2 (m, 5 H); IR (film) 2990, 2230, 983, 911, 750 cm^{-1}; MS, m/z 171 (M^+), 130 (M – 41). Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C, 84.19; H, 7.67.

***N,N*-Diethyl-3-phenyl-5-hexenamide (10a)**: A, 80%; NMR ($CDCl_3$) δ 1.05 (t, 6 H, J = 6 Hz), 2.4–2.9 (m, 5 H), 3.33 (q, 4 H, J = 6 Hz), 4.9–5.2 (m, 2 H), 5.4–5.9 (m, 1 H), 7.2 (br s, 5 H); IR (film) 3060, 3020, 2965, 2930, 1670, 1350, 1320, 1230, 1135, 1060, 910 cm^{-1}; MS, m/z 245 (M^+). Anal. Calcd for $C_{16}H_{23}NO$: C, 78.32; H, 9.44. Found: C, 78.61; H, 9.61.

Ethyl 3-(2-furyl)-5-hexenoate (11a): A, 83%; C, 26%; NMR ($CDCl_3$) δ 1.16 (t, 3 H, J = 6 Hz), 2.36 (t, 2 H, J = 7 Hz), 2.49 (d, 2 H, J = 7 Hz), 2.9–3.3 (m, 1 H), 3.9 (q, 2 H, J = 6 Hz), 4.7–4.9 (m, 2 H), 5.2–5.65 (m, 1 H), 5.75 (d, 1 H, J = 3 Hz), 5.9–6.0 (m, 1 H), 7.0 (br s, 1 H); IR (film) 2951, 1732, 1150, 982, 902 cm^{-1}; MS, m/z 208 (M^+), 167 (M – 41). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.33; H, 7.76.

1-(2-Furyl)-1,5-hexadien-3-one (11b): C, 22%; NMR ($CDCl_3$) δ 3.23 (d, 2 H, J = 7 Hz), 4.8–5.15 (m, 2 H), 5.5–6.2 (m, 1 H), 6.3–6.6 (m, 3 H), 7.2 (d, 1 H, J = 15 Hz), 7.35 (s, 1 H); IR (film) 3060, 2970, 2910, 1720, 1635, 1600, 1430, 1140, 1010, 900 cm^{-1}; MS, m/z 162 (M^+).

3-(2-Furyl)-5-hexenenitrile (12a): A, 91%; C, 73%; NMR ($CDCl_3$) δ 2.49 (t, 2 H, J = 6 Hz), 2.51 (d, 2 H, J = 6 Hz), 3.10 (q, 1 H, J = 6 Hz), 5.0–5.25 (m, 2 H), 5.4–5.9 (m, 1 H), 6.1 (d, 1 H, J = 3 Hz), 6.2–6.3 (m, 1 H), 7.1 (s, 1 H); IR (film) 2910, 2215, 982, 911, 728 cm^{-1}; MS, m/z 161 (M^+). Anal. Calcd for $C_{10}H_{11}N$: C, 82.72; H, 7.64. Found: C, 82.56; H, 7.68.

***N,N*-Diethyl-3-(2-furyl)-5-hexenamide (13a)**: A, 84%; NMR (CCl_4) δ 1.0–1.3 (m, 6 H), 2.25–2.6 (m, 4 H), 3.0–3.6 (m, 5 H), 4.75–5.15 (m, 2 H), 5.3–5.8 (m, 1 H), 5.88 (d, 1 H, J = 2 Hz), 6.05–6.15 (m, 1 H), 7.15 (m, 1 H); IR (film) 3070, 2970, 2940, 1640, 1440, 1380, 1225, 1150, 1020, 920, 900 cm^{-1}; MS, m/z 235 (M^+).

Ethyl 3-*tert*-butyl-5-hexenoate (14a): A, 80%; NMR ($CDCl_3$) δ 1.07 (s, 9 H), 1.21 (t, 3 H, J = 6 Hz), 1.7–2.4 (m, 5 H), 4.13 (q, 2 H, J = 6 Hz), 4.7–5.0 (m, 2 H), 5.3–5.8 (m, 1 H); IR (film) 2960, 1715, 980, 904 cm^{-1}; MS, m/z 198 (M^+).

7,7-Dimethyl-1,5-octadien-4-one (14b): C, 39%; NMR ($CDCl_3$) δ 1.06 (s, 9 H), 3.13 (d, 2 H, J = 6 Hz), 4.7–5.1 (m, 2 H), 5.5–6.0 (m, 2 H), 6.25 (AB q, 2 H, $\Delta\nu_{AB}$ = 75 Hz, J = 15 Hz); IR (film) 3080, 2970, 2870, 1680, 1630, 1430, 1370, 1080, 1000, 925, 800 cm^{-1}; MS, m/z 152 (M^+). Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.68; H, 10.24.

7,7-Dimethyl-4-(2-propenyl)-1,5-octadien-4-ol (14c): C, 39%; NMR ($CDCl_3$) δ 0.98 (s, 9 H), 2.20 (d, 4 H, J = 6 Hz), 3.2 (br s, 1 H), 4.7–5.0 (m, 4 H), 5.3–6.0 (m, 2 H), 6.25 (AB q, 2 H, $\Delta\nu_{AB}$ = 75 Hz, J = 15 Hz); IR (film) 3650–3150, 3080, 2930, 1640, 1460, 1260, 1050, 920, 820 cm^{-1}; MS, m/z 194 (M^+).

3-*tert*-Butyl-5-hexenenitrile (15a): A, 65%; C, 46%; NMR ($CDCl_3$) δ 1.0 (s, 9 H), 1.7–2.4 (m, 5 H), 4.9–5.2 (m, 2 H), 5.4–5.9 (m, 1 H); IR (film) 2990, 2232, 983, 910, 750, 690 cm^{-1}; MS, m/z 110 (M – 41).

16b and **16c** were identical with **14b** and **14c**, respectively.

Benzyl 5-hexenoate (17a): A, 65%; C, 28%; NMR ($CDCl_3$) δ 1.4–2.4 (m, 6 H), 4.8–5.1 (m, 4 H), 5.4–5.9 (m, 1 H), 7.30 (s, 5 H); IR (film) 2910, 1727, 1150, 740, 685 cm^{-1}; MS, m/z 204 (M^+). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.50; H, 7.94.

Diethyl 2-(2-propenyl)butanedioate (18a) [72140-08-0]:[41] A, 80%; C, 64%; NMR ($CDCl_3$) δ 1.23 (t, 6 H, J = 6 Hz), 2.1–2.8 (m, 4 H), 4.06 (q, 4 H, J = 6 Hz), 4.7–5.0 (m, 2 H), 5.2–5.75 (m, 1 H); IR (film) 2980, 1740, 1160, 982, 910 cm^{-1}; MS, m/z 169 (M – 45). Anal. Calcd for $C_9H_{14}O_4$: C, 56.41; H, 7.58. Found: C, 56.56; H, 7.54.

Benzyl 2-methyl-3-phenyl-5-hexenoate (19a): A, 80%; NMR ($CDCl_3$) δ 0.95 (d, 3 H, J = 6 Hz), 1.25 (t, 3 H, J = 6 Hz), 2.1–2.9 (m, 4 H), 4.4 (q, 2 H, J = 6 Hz), 4.7–5.0 (m, 2 H), 5.3–5.8 (m, 1 H), 7.1–7.5 (m, 5 H); IR (film) 2980, 1710, 1240, 1100, 755, 695 cm^{-1}; MS, m/z 232 (M^+).

2-Methyl-1-phenyl-1,5-hexadien-3-one (19b): C, 39%; NMR ($CDCl_3$) δ 2.00 (s, 3 H), 3.46 (d, 2 H, J = 6 Hz), 4.8–5.1 (m, 2 H), 5.6–6.1 (m, 1 H), 6.9–7.3 (m, 6 H).

4-[(*Z*)-1-Methyl-2-phenylethenyl]-1,6-hexadien-4-ol (19c): C, 9%; NMR ($CDCl_3$) δ 1.76 (s, 3 H), 2.00 (br s, 1 H), 2.2–2.6 (m, 4 H), 4.8–5.1 (m, 4 H), 5.4–6.9 (m, 2 H), 6.50 (s, 1 H), 6.9–7.3 (m, 5 H).

3-(2-Propenyl)-2-(ethoxycarbonyl)coumarin (20a): A, 91%; B, 49%;, C, 83%; NMR ($CDCl_3$) δ 1.03 (t, 3 H, J = 6 Hz), 2.30 (t, 2 H, J = 4 Hz), 3.15–3.4 (m, 1 H), 3.63 (d, 1 H, J = 5 Hz), 3.98 (q, 2 H, J = 6 Hz), 4.8–5.1 (m, 2 H), 5.3–5.85 (m, 1 H), 6.7–7.1 (m, 4 H); IR (film) 2970, 1775, 1735, 1220, 1160 cm^{-1}; MS, m/z 260 (M^+).

Ethyl 3-methyl-5-hexenoate (21a) [63473-84-7]:[41] A, 19%; NMR ($CDCl_3$) δ 0.9–1.0 (m, 3 H), 1.25 (t, 3 H, J = 6 Hz), 1.75–2.4 (m, 5 H), 4.15 (q, 2 H, J = 6 Hz), 4.7–5.0 (m, 2 H), 5.3–5.8 (m, 1 H); IR (film) 3080, 2950, 1740, 1640, 1460, 1380, 1040, 1000, 920 cm^{-1}; MS, m/z 156 (M^+).

1,5-Heptadien-4-one (21b): C, 31%; NMR ($CDCl_3$) δ 2.2 (d, 3 H, J = 5 Hz), 3.2–3.5 (m, 2 H), 4.7–5.0 (m, 2 H), 4.7–5.0 (m, 2 H), 5.3–5.9 (m, 3 H).

Benzyl 3,3-dimethyl-5-hexenoate (22a): C, 27%; NMR ($CDCl_3$) δ 1.80 (s, 6 H), 2.10 (s, 2 H), 2.0–2.4 (m, 4 H), 4.8–5.1 (m, 4 H), 5.4–5.9 (m, 1 H), 7.03 (s, 5 H); IR (film) 2900, 1715, 1220, 1130, 905 cm^{-1}; MS, m/z 232 (M^+).

Ethyl 3-methyl-3-phenyl-5-hexenoate (23a): A, 47%; NMR ($CDCl_3$) δ 1.03 (t, 3 H, J = 6 Hz), 1.4 (s, 3 H), 2.4–2.8 (m, 4 H), 4.0 (q, 2 H, J = 6 Hz), 4.7–5.0 (m, 2 H), 5.3–5.8 (m, 1 H), 7.2 (br s, 5 H); IR (film) 3050, 2970, 1720, 1625, 1440, 1360, 1340, 1270, 1040, 875, 700 cm^{-1}; MS, m/z 191 (M – 41).

6-Phenyl-1,5-heptadien-4-one (23b): C, 64%; NMR ($CDCl_3$) δ 2.50 (s, 3 H), 3.2 (d, 2 H, J = 6 Hz), 4.8–5.1 (m, 2 H), 5.5–6.0 (m, 1 H), 6.0 (br s, 1 H), 7.0–7.4 (m, 5 H); IR (film) 2960, 1705, 1151, 740, 680 cm^{-1}; MS, m/z 186 (M^+).

1,2-Adduct (24b): C, 31%; NMR ($CDCl_3$) δ 0.82 (s, 9 H), 1.4–2.4 (m, 1 H), 3.13 (d, 2 H, J = 6 Hz), 4.9–5.2 (m, 2 H), 5.5–6.1 (m, 2 H), 5.95 (br s, 1 H); IR (film) 3070, 2950, 2870, 1700, 1640, 1460, 1370, 1270, 1195, 1180, 1145, 1040, 920 cm^{-1}; MS, m/z 220 (M^+).

Diethyl 2-(1,1-dimethyl-3-butenyl)propanedioate (25a) [32119-46-3]:[41] A, 52%; B, 35%; C, 86%; NMR ($CDCl_3$) δ 1.06 (s, 6 H), 1.23 (t, 6 H, J = 6 Hz), 2.0–2.25 (m, 2 H), 3.10 (s, 1 H), 4.06 (q, 4 H, J = 6 Hz), 4.8–5.1 (m, 2 H), 5.5–5.9 (m, 1 H); IR (film) 3080, 2975, 1760, 1720, 1640, 1365, 1040, 920, 860 cm^{-1}; MS, m/z 242 (M^+), 201 (M – 41). Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 64.20; H, 9.04.

Benzyl 2-(2-propenyl)cyclopentane-1-carboxylate (26a): A, 50%; C, 15%; NMR ($CDCl_3$) δ 1.3–2.3 (m, 10 H), 4.5–5.1 (m, 4 H), 5.2–5.8 (m, 1 H), 7.2 (s, 5 H); IR (film) 2940, 1713, 1256, 1079, 731, 689 cm^{-1}; MS, m/z 244 (M^+).

1-(1-Oxo-3-butenyl)cyclopentene (26b): C, 25%; NMR ($CDCl_3$) δ 1.6–2.0 (m, 2 H), 2.1–2.3 (m, 4 H), 4.7–5.0 (m, 2 H), 5.3–5.8 (m, 1 H), 7.0–7.2 (br s, 1 H).

2-(2-Propenyl)cyanocyclopentane (27a): A, 44%; C, 23%; NMR ($CDCl_3$) δ 1.6–2.8 (m, 10 H), 4.7–5.0 (m, 2 H), 5.3–5.7 (m, 1 H); IR (film) 3070, 2230, 1640, 1445, 920 cm^{-1}; MS, m/z 135 (M^+), 94 (M – 41). Anal. Calcd for $C_9H_{13}N$: C, 79.94; H, 9.69. Found: C, 79.72; H, 10.05.

2-Acetyl-3-(2-propenyl)coumarin (28a): A, 22%; B, 79%; NMR ($CDCl_3$) δ 2.12 (s, 3 H), 2.30 (t, 2 H, J = 6 Hz), 3.6–3.8 (m, 2 H), 4.8–5.2 (m, 2 H), 5.4–5.9 (m, 1 H), 7.0–7.4 (m, 5 H); IR (film) 3020, 2925, 2850, 1740, 1700, 1600, 1560, 1460, 1370, 1210 cm^{-1}; MS, m/z 189 (M – 41).

1-Phenyl-1,5-hexadien-3-ol (29b) [13891-95-7]:[41] A, 86%; C, 86%; NMR ($CDCl_3$) δ 2.29 (t, 2 H, J = 6 Hz), 3.00 (br s, 1 H), 4.15 (q, 1 H, J = 6 Hz), 4.7–5.1 (m, 2 H), 5.3–5.9 (m, 1 H), 5.90 (dd, 1 H, J = 15 Hz, 4 Hz), 6.4 (d, 1 H, J = 15 Hz), 6.8–7.2 (m, 5 H); IR (film) 3650–3100, 3080, 3025, 2935, 1640, 1600,1500, 1450, 965, 920, 745, 690 cm^{-1}; MS, m/z 156 (M – 18).

2-Methyl-1-phenyl-1,5-hexadien-3-ol (30b): A, 90%; C, 81%; NMR ($CDCl_3$) δ 1.85 (s, 3 H), 2.37 (t, 2 H, J = 7 Hz), 3.6 (br s, 1 H), 4.1 (t, 1 H, J = 7 Hz), 4.8–5.2 (m, 2 H), 5.5–6.0 (m, 1 H), 6.35 (br s, 1 H), 7.15 (s, 5 H); IR (film) 3650–3100, 3080, 2975,

2920, 1640, 1600, 1495, 1440, 1380, 920, 755, 700 cm^{-1}; MS, m/z 170 (M − 18), 147 (M − 41).

3-Methyl-6-phenyl-8-nonen-4-one (31a): A, 57%; B, 74%; C, 17%; NMR ($CDCl_3$) δ 0.71–1.05 (m, 6 H), 2.1–2.3 (m, 2 H), 2.7 (d, 2 H, J = 6 Hz), 3.26 (t, 1 H, J = 6 Hz), 4.65–4.95 (m, 2 H), 5.3–5.65 (m, 1 H), 6.8–7.4 (m, 5 H); IR (film) 2960, 1710, 905, 742, 690 cm^{-1}; MS, m/z 230 (M$^+$).

3-Methyl-4-[(*E*)-2-phenylethenyl]-1-hepten-4-ol (31b): A, 20%; C, 6%; NMR ($CDCl_3$) δ 0.9–1.6 (m, 14 H), 2.15–2.3 (m, 4 H), 4.7–5.0 (m, 2 H), 5.2–5.8 (m, 1 H), 6.12 (AB q, 2 H, $\Delta\nu_{AB}$ = 36 Hz, J = 15 Hz), 6.8–7.3 (m, 5 H); IR (film) 3500, 2960, 970, 905, 738, 688 cm^{-1}; MS, m/z 230 (M$^+$).

2,2-Dimethyl-5-phenyl-7-octen-3-one (32a): A, 58%; B, 92%; C, 45%; NMR ($CDCl_3$) δ 0.96 (s, 9 H), 2.21 (t, 2 H, J = 5 Hz), 2.56 (d, 2 H, J = 7 Hz), 3.0–3.3 (m, 1 H), 4.7–5.0 (m, 2 H), 5.2–5.7 (m, 1 H), 6.9–7.3 (m, 5 H); IR (film) 2942, 1708, 989, 906, 790, 690 cm^{-1}; MS, m/z 230 (M$^+$).

3-*tert*-Butyl-1-phenyl-1,5-hexadien-3-ol (32b): A, 26%; C, 43%; NMR ($CDCl_3$) δ 0.96 (s, 9 H), 1.6 (br s, 1 H), 2.2–2.4 (m, 2 H), 4.8–5.0 (m, 2 H), 5.3–5.9 (m, 1 H), 6.30 (AB q, 2 H, $\Delta\nu_{AB}$ = 24 Hz, J = 15 Hz), 7.0–7.4 (m, 5 H); IR (film) 3550, 2960, 974, 911, 735, 689 cm^{-1}; MS, m/z 230 (M$^+$).

5-Phenyl-3,7-octadienenitrile (1,6-adduct, 33a): C, 80%; NMR ($CDCl_3$) δ 2.36 (t, 2 H, J = 6 Hz), 2.83 (d, 2 H, J = 6 Hz), 3.1–3.4 (m, 1 H), 4.70–5.90 (m, 5 H), 6.8–7.2 (m, 5 H); IR (film) 3070, 3020, 2920, 2240, 1675, 1600, 1590, 1420, 1080, 990, 906, 751 cm^{-1}; MS, m/z 197 (M$^+$), 156 (M − 41). Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66. Found: C, 85.14; H. 7.67.

3-[(*E*)-2-Phenylethenyl]-5-hexenenitrile (1,4-adduct, 33b): A, 37%; NMR ($CDCl_3$) δ 2.2–2.7 (m, 4 H), 4.9–5.2 (m, 2 H), 5.4–5.9 (m, 1 H), 6.0 (dd, 1 H, J = 15 Hz, 12 Hz), 6.35 (d, 1 H, J = 15 Hz), 7.0–7.3 (m, 5 H); IR (film) 3070, 3020, 2910, 2225, 1640, 1620, 1600, 1595, 1450, 1000, 970, 920 cm^{-1}; MS, m/z 197 (M$^+$). Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66. Found: C, 85.21; H, 7.68.

Ethyl 5-phenyl-3,7-octadienoate (1,6-adduct, 34a): C, 95%; NMR ($CDCl_3$) δ 1.28 (t, 3 H, J = 6 Hz), 2.39 (t, 2 H, J = 6 Hz), 2.86 (d, 2 H, J = 6 Hz), 3.23 (q, 1 H, J = 6 Hz), 3.9 (q, 2 H, J = 6 Hz), 4.7–5.0 (m, 2 H), 5.2–5.7 (m, 3 H), 7.0 (br s, 5 H); IR (film) 3070, 3030, 2980, 1730, 1640, 1600, 1495, 1455, 1370, 1030, 975, 920, 700 cm^{-1}; MS, m/z 244 (M$^+$), 203 (M − 41).

Ethyl 3-[(*E*)-2-phenylethenyl]-5-hexenoate (1,4-adduct, 34b): A, 63%; NMR ($CDCl_3$) δ 1.17 (t, 3 H, J = 6 Hz), 2.20–2.60 (m, 5 H), 4.0 (q, 2 H, J = 6 Hz), 4.9–5.3 (m, 2 H), 5.3–6.3 (m, 3 H), 7.0–7.2 (m, 5 H); IR (film) 3080, 3025, 2980, 1735, 1640, 1600, 1495, 1370, 1015, 965, 920 cm^{-1}; MS, m/z 203 (M − 41).

Methyl 5-methyl-3,7-octadienoate (1,6-adduct, 35a) [77291-11-3]:[41] C, 61%;, NMR ($CDCl_3$) δ 0.97 (d, 3 H, J = 6 Hz), 1.9–2.2 (m, 3 H), 2.89 (d, 2 H, J = 6 Hz), 3.57 (s, 3 H), 4.8–5.0 (m, 2 H), 5.3–5.8 (m, 3 H).

Methyl 3-(2-propenyl)-4-hexenoate (1,4-adduct, 35b): A, 31%; NMR ($CDCl_3$) δ 1.62 (d, 3 H, J = 6 Hz), 2.2–3.0 (m, 5 H), 3.57 (s, 3 H), 4.7–5.0 (m, 2 H), 5.3–5.6 (m, 3 H).

Acknowledgment. Dr. Ada Casares was on sabbatical leave (1981–1982) from the Facultad De Quimica, Mexico. This research was supported by a grant from the Research Corporation. Special thanks are extended to Ms. Leslie Sykes, Mr. Ken Hull, and Mr. Richard Fishman (UGA undergraduates) for assistance in the preparation of numerous Michael acceptors.

Registry No. (*E*)-**7**, 1896-62-4; **7a**, 69492-29-1; (*E*)-**7b**, 100840-12-8; (*E*)-**8**, 1754-62-7; **8a**, 52129-50-7; (*E*)-**8b**, 100840-13-9; (*E*)-**9**, 1885-38-7; **9a**, 87995-21-9; (*E*)-**10**, 27829-46-5; **10a**, 87995-22-0; (*E*)-**11**, 53282-12-5; **11a**, 100840-14-0; (*E*)-**11b**, 100840-15-1; (*E*)-**12**, 6125-63-9; **12a**, 100840-16-2; (*E*)-**13**, 88312-33-8; **13a**, 100840-17-3; (*E*)-**14**, 22147-62-2; **14a**, 87995-25-3; (*E*)-**14b**, 100840-18-4; (*E*)-**14c**, 100840-19-5; (*E*)-**15**, 29582-19-2; **15a**, 87995-26-4; (*E*)-**16**, 100840-11-7; (*E*)-**17**, 2495-35-4; **17a**, 87995-27-5; (*E*)-**18**, 623-91-6; **18a**, 72140-08-0; (*E*)-**19**, 7042-33-3; **19a**, 87995-36-6; (*E*)-**19b**, 100840-20-8; (*Z*)-**19c**, 100840-21-9; **20**, 1846-76-0; **20a**, 87995-41-3; (*E*)-**21**, 623-70-1; **21a**, 63473-84-7; (*E*)-**21b**, 33698-63-4; **22**, 638-10-8; **22a**, 87995-46-8; (*E*)-**23**, 1504-72-9; **23a**, 100840-22-0; (*E*)-**23b**, 100840-23-1; **24**, 13733-50-1; **24b**, 100840-24-2; **25**, 6802-75-1; **25a**, 32119-46-3; **26**, 87995-31-1; **26a**, 87995-37-7; **26b**, 84599-56-4; **27**, 3047-38-9; **27a**, 87995-38-8; **28**, 3949-36-8; **28a**, 87995-40-2; (*E*)-**29**, 14371-10-9; (*E*)-**29b**, 79299-29-9; (*E*)-**30**, 15174-47-7; (*E*)-**30b**, 100840-25-3; (*E*)-**31**, 84319-68-6; **31a**, 87995-33-3; (*E*)-**31b**, 87995-42-4; (*E*)-**32**, 29569-91-3; **32a**, 87995-34-4; (*E*)-**32b**, 100840-26-4; (*E,E*)-**33**, 53649-66-4; (*E*)-**33a**, 100840-27-5; (*E*)-**33b**, 100840-28-6; (*E,E*)-**34**, 39806-16-1; (*E*)-**34a**, 100840-29-7; (*E*)-**34b**, 100857-97-4; (*E,E*)-**35**, 2396-84-1; i, 38868-10-9; ii, 25117-54-8; ethyl (*E*)-5-methyl-3,7-octadienoate, 100840-30-0; ethyl (*E*)-3-(2-propenyl)-4-hexenoate, 100840-31-1; lithium diallylcuprate diethyl[(*N,N*-diethylcarbamoyl)methyl]-phosphate, 21500-57-2; anion, 100840-10-6; cyclopentanone cyanohydrin, 5117-85-1; 3-furfural, 498-60-2; trimethylacetaldehyde, 630-19-3; benzaldehyde, 100-52-7; carbomethoxymethylenetriphenylphosphorane, 2605-67-6; diethyl malonate, 105-53-3; acetone, 67-64-1; acetophenone, 98-86-2; 4-*tert*-butylcyclohexanone, 98-53-3; 1-cyclopentenecarboxylic acid, 1560-11-8; methacrylic acid, 79-41-4; cinnamaldehyde, 104-55-2; *sec*-butyllithium, 598-30-1; $TiCl_4$, 429-41-4.

Allylsilane-Initiated Cyclopentane Annulations[1]

George Majetich,* Richard W. Desmond, Jr., and José J. Soria

School of Chemical Sciences, Department of Chemistry, The University of Georgia, Athens, Georgia 30602

Received September 12, 1985

The utility of intramolecular allylsilane additions to various Michael acceptors for achieving cyclopentane annulation is reported. Our results revealed that fluoride ion catalysis annulated both acyclic and cyclic systems, while Lewis acid catalyses ($TiCl_4$, $EtAlCl_2$, BF_3·Et_2O) were ineffective. This divergence in reactivity is rationalized in terms of conformational and stereoelectronic effects.

Polycyclic natural products containing cyclohexanoid and cyclopentanoid systems have inspired many creative procedures for carbocyclic ring formation. Although the cyclization of cationic, radical, and stabilized anionic species can efficiently generate six-membered rings, it was soon established that such conventional methods are not always applicable to five-membered rings. Consequently, the development of versatile methods for cyclopentane annulation has been the subject of considerable activity.[2]

Chart I illustrates several known annulation procedures in which five-membered rings result from the intramo-

(1) This work was presented in part at the 6th Gulf Coast Conference at Pensacola, FL, in Sept 1983, and at the 35th SERMC at Raleigh, NC, in Oct 1983, and taken in part from the M.S. Thesis of Mr. Richard Desmond, University of Georgia, 1984.

(2) For two recent reviews see: (a) Ramaiah, M. *Synthesis* **1984**, 529. (b) Paquette, L. A. *Top. Curr. Chem.* **1984**, *119*, 1.

0022-3263/86/1951-1753$01.50/0