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1 AUTHOR:

T. V. Rajanbabu
The Ohio State University
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Addition of Ketene Trimethylsilyl Acetals to α,β-Unsaturated Ketones: A New Strategy for Michael Addition of Ester Enolates†

T. V. RajanBabu

Central Research & Development Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Delaware 19898

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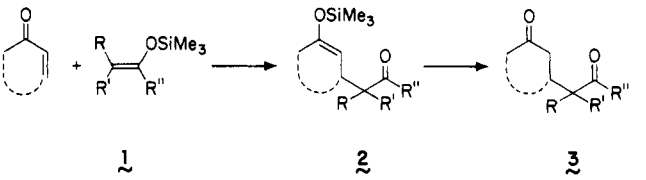
Trialkylsilyl ketene acetals in the presence of tris(dimethylamino)sulfonium difluorotrimethylsiliconate generate very potent carbon nucleophiles formally equivalent to ester enolates. In sharp contrast to the commonly used lithium enolates, these acetals add to α,β-unsaturated ketones in exclusive 1,4 fashion to give 5-(trialkylsiloxy)-4-pentenoic acid esters in excellent yields. The addition is nonstereoselective with respect to the newly created chiral centers. These adducts can be further alkylated in situ, thus generating two C–C bonds in one pot, or they can be hydrolyzed to 1,5-dicarbonyl compounds. Unhindered silyl ketene acetals also add to enones in nitromethane at room temperature even in the absence of fluoride ion: the reaction is accompanied by an intermolecular migration of silicon promoted by the highly polar solvent. Trimethylsilyl chloride is a catalyst for the additions of otherwise unreactive hindered silyl ketene acetals. Mechanisms for both fluoride-catalyzed and solvent-assisted additions are proposed.

The Michael reaction is a well-known, important method for carbon–carbon bond formation.[1-4] However, its synthetic use is limited essentially to the additions of stabilized anions such as those derived from malonates, cyanoacetates, and acetoacetates. The reactions with simple, unstabilized enolates are often complicated by attendant side reactions, which include proton transfers, undesired condensations between reacting species, and concomitant 1,2 additions. Some of these problems can be overcome by the use of modified enolates[1c,4a] or by the use of masked carbonyl functionality.[1e] Yet another approach is to use silyl enol ethers as functional equivalents of enolates (Scheme I). For example, *O*-trimethylsilyl enol ethers **1** add to α,β-unsaturated ketones[2a] and nitro compounds[2b] in good yields in the presence of Lewis acids ($TiCl_4$, Ti(*i*-PrO)$_4$, and $SnCl_4$). A heterogeneous CsF-catalyzed addition of silyl enol ethers has also been reported.[3] With Lewis acid or CsF catalysis, however, the valuable intermediate silyl enol ethers **2** cannot be isolated. To date, the only reported case in which the silyl enol ether intermediate has been isolated is the reaction between the trimethylsilyl enol ether of *S*-*tert*-butyl thioacetate and cyclopentenone, promoted by tetra-*n*-butylammonium fluoride.[4a]

In this study, we have focused our attention on the reactions of trimethylsilyl ketene acetals **1** (R″ = *O*-alkyl) with α,β-unsaturated ketones catalyzed by a Lewis base. One may anticipate that appropriate Lewis base catalysts not only enhance the nucleophilicity of **1** but also do so without increasing its basicity. Thus, some of the side reactions encountered with conventional and highly basic metal enolates may be circumvented. Furthermore, the silylated 1,4 adducts may be stable under reaction con-

Scheme I



1 **2** **3**

† Contribution No. 3367.

(1) (a) Bergmann, E. D.; Ginsburg, D.; Pappo, R. *Org. React.* **1959**, *10*, 179. (b) House H. O. "Modern Synthetic Reactions", 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; p 595. (c) Krief, A. *Tetrahedron* **1980**, *36*, 2531 for an exhaustive review of Michael additions of modified enolates. (d) Schultz, A. G.; Yee, Y. K. *J. Org. Chem.* **1976**, *25*, 4044. (e) For, e.g.: Herrmann, J. L.; Kiecykowski, G. R.; Romanet, R. F.; Wepplo, P. J.; Schlessinger, R. H. *Tetrahedron Lett.* **1973**, 4711. (f) Fang, J. M. *J. Org. Chem.* **1982**, *47*, 3464 and references cited therein. (g) For kinetic 1,4 addition of dithioacetate enolate see: Metzner, P. *J. Chem. Soc., Chem. Commun.* **1982**, 335.

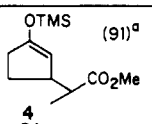
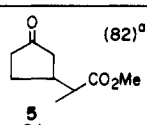
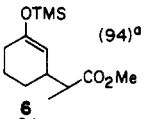
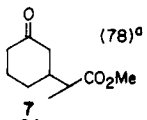
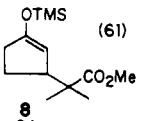
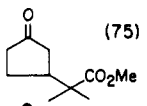
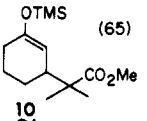
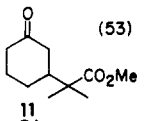
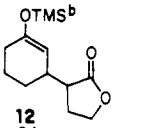
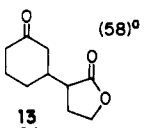
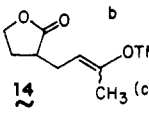
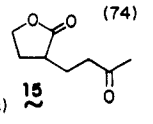
(2) (a) Narasaka, K.; Soai, K.; Mukaiyama, T. *Chem. Lett.* **1974**, 1223. Saigo, K.; Osaki, M.; Mukaiyama, T. *Ibid.* **1976**, 163. Chan, T. H.; Brownbridge, P. *J. Chem. Soc., Chem. Commun.* **1979**, 578. Matsuda, I.; Murata, S.; Izuma, Y. *J. Org. Chem.* **1980**, *45*, 237. (b) Miyashita, M.; Yanami, Y.; Yoshikoshi, A. *J. Am. Chem. Soc.* **1976**, *98*, 4679.

(3) Boyer, J.; Corriu, R. J. P.; Perz, R.; Reye, C. *J. Organomet. Chem.* **1980**, *184*, 157. Boyer, J.; Corriu, R. J. P.; Perz, R.; Reye, C. *J. Chem. Soc., Chem. Commun.* **1981**, 122. Boyer, J.; Corriu, R. J. P.; Perz, R.; Reye, C. *Tetrahedron* **1983**, *39*, 117.

(4) (a) Gerlach, H.; Kunzler, P. *Helv. Chim. Acta* **1978**, *61*, 2503. (b) Thio ester enolates add 1,2 or 1,4 depending on the Michael acceptor and reaction conditions. See ref 4a and: Shenvi, A. B.; Gerlach, H. *Helv. Chim. Acta* **1980**, *63*, 2426.

0022-3263/84/1949-2083$01.50/0

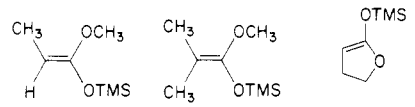
Table I. TASF-Catalyzed Additions of Trimethylsilyl Ketene Acetals to α,β-Unsaturated Ketones

entry	silyl ketene acetal	enone	products (isolated yield, %): adduct	products (isolated yield, %): after hydrolysis
1	1a	CYCLOPENTENONE	 (91)[a]	 (82)[a]
			4	5
2	1a	CYCLOHEXENONE	 (94)[a]	 (78)[a]
			6	7
3	1b	CYCLOPENTENONE	 (61)	 (75)
			8	9
4	1b	CYCLOHEXENONE	 (65)	 (53)
			10	11
5	1c	CYCLOHEXENONE		 (58)[a]
			12	13
6	1c	METHYL VINYL KETONE		 (74)
			14	15

[a] 1:1 mixture of diasteriomers. [b] Primary adduct not isolated.

ditions and amenable to isolation. Indeed, we have found that tris(dimethylamino)sulfonium difluorotrimethylsiliconate (TASF)[5,6] is an excellent catalyst for the Michael addition, as Noyori has found for aldol condensation,[5a] and more importantly, the catalyst fulfills the expectations mentioned above. During the course of the study, we have also found that the addition proceeds in some cases even without catalyst at room temperature.[7] These data as well as the stereochemistry of the addition and related results pertinent to the mechanism will be described.

TASF-Catalyzed Additions. Ketene trimethylsilyl acetals **1a–c** add to α,β-unsaturated ketones in the presence of catalytic amounts of TASF to give 5-(trimethylsiloxy)-4-pentenoic acid esters **2** (R″ = *O*-alkyl). As summarized in Table I, the yields are high, and the addition proceeds exclusively in the 1,4 fashion. It should be noted that additions producing quarternary carbon atoms proceed in equally high yields (entries 3 and 4). The product silyl enol ethers **2** can be readily hydrolyzed to the respective 4-acylbutanoic acid esters **3** (R″ = *O*-alkyl).

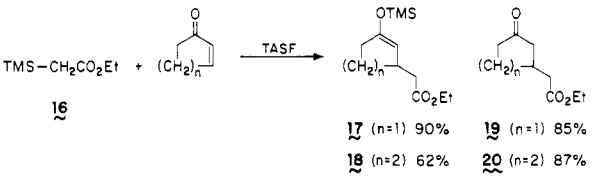


1a **1b** **1c**

Typically, an equimolar mixture of the ketene silyl acetal and the enone in THF is added to a stirred solution of 0.05–0.10 molar equiv of TASF in THF or THF/acetonitrile.[8] After the mixture was stirred for an appropriate time, the product is isolated by partitioning between hexane and water or by simply removing the solvent after the catalyst has been quenched with acetic acid. The hydrolysis to the corresponding 4-acylbutanoate derivatives **3** is carried out by stirring a methylene chloride solution of **2** with silica gel impregnated with oxalic acid (6% aqueous solution).

Diastereoselection potentially achievable in the additions of **1a** and **1c** is very low. For example, **1a** adds to cyclopentenone to afford a 1:1 mixture of diastereomers **4** in 91% yield (entry 1). The 360-MHz NMR spectrum of **4** shows the doubling of the peaks due to $SiCH_3$'s (δ 0.15 (s, separated by 5 Hz)), CH_3CH (δ 1.05 (2d, J = 6 Hz, separation 4 Hz)), CH_3O (δ 3.60 (2s, separation 1 Hz)), and the olefinic proton (δ 4.45 and 4.55 (2m, br, separation 36 Hz)). The NMR spectrum of the keto ester **5** shows the same type of splitting for the two CH_3 groups. Cyclohexanone adducts **6** and **7** also show similar patterns.

The *C*-silyl compound ethyl (trimethylsilyl)acetate (**16**) also participates in the reaction. It is not surprising because the Me_3Si group in **16** is known to be displaced by fluoride ion.[9] Hydrolysis of adducts **17** and **18** give **19** and **20** in 85% and 87% yields, respectively (eq 1).



16

17 (n=1) 90% **19** (n=1) 85%

18 (n=2) 62% **20** (n=2) 87%

Solvent-Assisted Additions. During the course of this study, we discovered that if nitromethane is used as the solvent, several additions readily proceed at *room temperature* without additional catalyst.[7] The results are summarized in Table II. Since similar, uncatalyzed additions of silyl ketene acetals in hot acetonitrile have been

(5) (a) Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1983**, *105*, 1598 and references cited therein. (b) Middleton, W. J. U.S. Patent 3 940 402, 1976. Submitted to Org. Syntheses. Tris(dimethylamino)-sulfonium difluorotrimethylsiliconate is prepared by mixing stoichiometric amounts of (dimethylamino)trimethylsilane and sulfur tetrafluoride in ether at −78 °C, stirring for 3 days at room temperature, and filtering off the solid product.

(6) In this study we intentionally avoided using the commonly available organic soluble fluorides such as tetra-*n*-butylammonium fluoride since they are invariably contaminated with water and attempts to get them absolutely anhydrous result in their decomposition: Sharma, R. K.; Fry, J. L. *J. Org. Chem.* **1983**, *48*, 2112. We thank Professor Fry for a preprint of his work. See also: Clark, J. H. *Chem. Rev.* **1980**, *80*, 429 for a review of the uses of various fluorides.

(7) While this work was in progress, Tamura et al. reported similar reactions in acetonitrile at higher temperature: (a) Kita, Y.; Segawa, J.; Haruta, J.; Fujii, T.; Tamura, Y. *Tetrahedron Lett.* **1980**, *21*, 3779. (b) Kita, Y.; Segawa, J.; Haruta, J.; Yasuda, H.; Tamura, Y. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1099.

(8) Tris(dimethylamino)sulfonium difluorotrimethylsiliconate is only partly soluble in THF at low temperatures. However, this has no effect on the yield of the reaction.

(9) (a) Noyori, R.; Yokoyama, K.; Sakata, J.; Kuwajima, I.; Nakamura, E.; Shimizu, M. *J. Am. Chem. Soc.* **1977**, *99*, 1265. (b) Nakamura, E.; Shimizu, M.; Kuwajima, I.; Sakata, J.; Yokoyama, K.; Noyori, R. *J. Org. Chem.* **1983**, *48*, 932.

(10) (a) Noyori, R.; Nishida, I.; Sakata, J. *Tetrahedron Lett.* **1980**, *21*, 2085. (b) Kuwajima, I.; Nakamura, E.; Shimizu, M. *J. Am. Chem. Soc.* **1982**, *104*, 1025.

(11) Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1981**, *103*, 2106.

(12) Ionic enolates have been made under conditions far different from those of additions. See, for example: Noyori, R.; Nishida, I.; Sakata, J.; Nishizawa, M. *J. Am. Chem. Soc.* **1980**, *102*, 1223 and ref 5a.

(13) (a) Evans, D. A.; McGee, L. R. *Tetrahedron Lett.* **1980**, *21*, 3975. Yamamoto, Y.; Maruyama, K. *Ibid.* **1980**, *21*, 4607. (b) Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1981**, 162. (c) Reetz, M. T.; Peter, R. *Tetrahedron Lett.* **1981**, *22*, 4691.

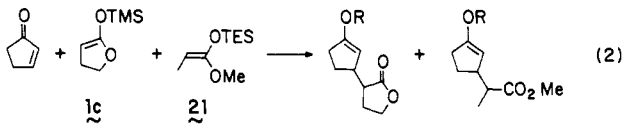
(14) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.

described recently by Tamura and co-workers,[7] we will limit our discussion to new aspects of this reaction.

The uncatalyzed and fluoride-catalyzed additions have similar stereochemical outcomes. Irrespective of the geometry of the starting enol ether, a 1:1 mixture of diastereomers is obtained (Table II, entries 1, 2, 6, 7, and 8). The structural proof comes from high-resolution NMR spectra (vide supra) of the silyl enol ether intermediates and of the final hydrolyzed products. For example, in adduct **24** the olefinic protons appear as broad singlets at δ 4.33 and 4.68 in a ratio of 1:1. The trimethylsilyl protons appear as two singlets of equal intensity around δ 0.15 separated by 1 Hz. The substituents on silicon (trimethyl vs. triethyl) do not have any effect either on the stereochemistry or yield of the reaction (Table II, entries 1 and 6).

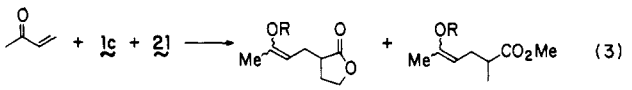
In sharp contrast to the fluoride-catalyzed reaction discussed earlier, the more hindered ketene acetal **1b** and ethyl (trimethylsilyl)acetate (**16**) failed to react with enones, even under forcing conditions. Bis(silyl) ketene acetals also fail to react (Table II, entries 9 and 10). However, the resistance to the generation of the quaternary center (entry 4) can be circumvented by the use of trimethylsilyl chloride as a catalyst in nitromethane (entry 5).

Mechanistically, it is important to note that a crossover experiment of **1c** and **21** with cyclopentenone yields all possible products, **4**, **23**, **24**, and **30**, in 89% yield based on the enone (eq 2). Methyl vinyl ketone reacts similarly to



(2)

R = TMS **24** 32% **4** 18%
R = TES **30** 21% **23** 29%

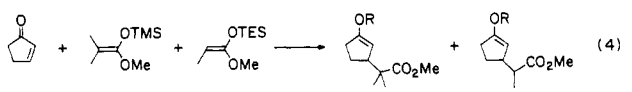


(3)

R = TMS **14** 21% **22** 23%
R = TES **32** 10% **31** 46%

give cis and trans isomers of **14**, **22**, **31**, and **32** in 73% yield (eq 3). The ratios do not change appreciably in nitromethane or acetonitrile, although the reactions are faster in nitromethane. Since control experiments show that silyl group exchange does not occur either between **1c** and **21** in the absence of the enones or among the adducts under the reaction conditions, the exchange must be an integral part of the reactions. In these and the following runs, the product ratios were determined by GLPC and GC–mass spectrometry.

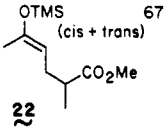
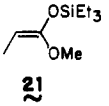
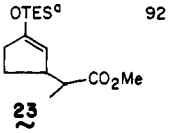
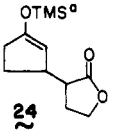
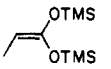
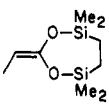
We have also found that the reaction of a more hindered ketene acetal **1b** with cyclopentanone does not proceed thermally even under forcing conditions (Table II, entry 4) but does take place if a less hindered ketene acetal, e.g., **21** is added. An exothermic reaction (eq 4) ensues at room temperature in acetonitrile giving four products **4**, **8**, **23**, and **33** in 36% yield after 20 h.



(4)

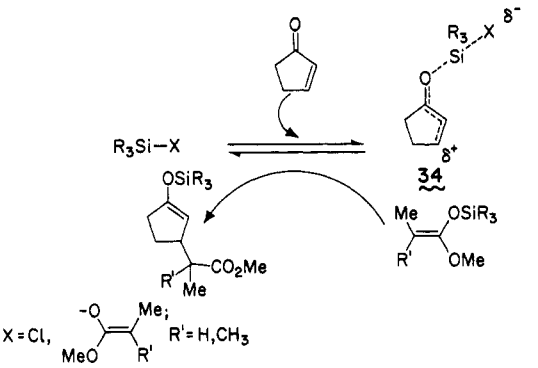
R = TMS **8** 13% **4** 12%
R = TES **33** 36% **23** 39%

Table II. Thermal Additions of Trimethylsilyl Ketene Acetals to α,β-Unsaturated Ketones

entry	ketene acetal	enone	product	yield, %
1	**1a**	CYCLOPENTENONE	**4**[a]	82
2	**1a**	CYCLOHEXENONE	**6**[a]	58
3	**1a**	METHYL VINYL KETONE	 (cis + trans) **22**	67
4	**1b**	CYCLOPENTENONE	**8**	<5
5	**1b** + TMSCl	"	**8**	67
6	 **21**	"	 **23**	92
7	**1c**	CYCLOPENTENONE	 **24**	48
8	**1c**	CYCLOHEXENONE	**12**[a]	46
9		CYCLOPENTENONE	NO REACTION	-
10		CYCLOPENTENONE	NO REACTION	-

[a] 1:1 mixture of diastereomers.

Scheme II

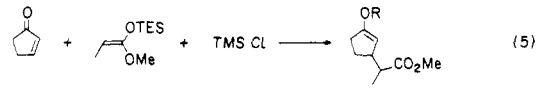


These observations suggest that silyl ketene acetals behave much like a Lewis acid and activate the enone for nucleophilic addition. This behavior is similar to the catalysis by trimethylsilyl triflate in several reactions of silyl enol ethers[15] (Scheme II). In our case, unhindered ketene acetals, e.g., **1c** and **21** complex with the enone, but hindered ones such as **1b** do not. The activated enone then reacts with silyl ketene acetal giving rise to the adducts as well as to silyl group exchange between the ketene acetals. An implication of this mechanism is that even in the simpler reactions listed in Table II, the reactive silyl ketene acetals such as **1a**, **1c**, or **21** function not only as a reaction component but also as an enone activator.

To further test this hypothesis, we have examined the effects of trimethylsilyl chloride on the reactions. The reaction of the Et_3Si ketene acetal with cyclopentenone in the presence of Me_3SiCl yields the silyl group exchanged

(15) Noyori, R.; Murata, S.; Suzuki, M. *Tetrahedron* **1981**, *37*, 3899.

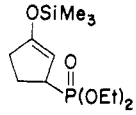
products **4** and **23** in 67% yield (eq 5). Interestingly, the



(5)

4 R = TMS 19%
23 R = TES 81%

Et_3Si adduct **23** predominates even if 2 equiv of Me_3Si are used in this reaction. This raises the possibility that under the reaction conditions, Me_3SiCl activates enones less efficiently than the unhindered silyl ketene acetals. Nevertheless, the sluggish reaction of cyclopentenone with a hindered ketene acetal **1b** (Table II, entry 4) is accelerated by Me_3SiCl (Table II, entry 5). The reaction is rapid in nitromethane, is much slower in acetonitrile, and is not observed in THF or methylene chloride. The remarkable solvent effect is consistent with the involvement of charge separated intermediates such as **34** in Scheme II. It is interesting to note that neither bis(silyl) ketene acetals (Table II, entries 9 and 10) nor C-silated esters **16** are sufficiently reactive as activator–nucleophile combinations. Solvent effects in the 1,4 addition of R_3SiOPX_2 (R = CH_3; X = OMe, OEt, NMe_2) to α,β-unsaturated ketones[16] have also been explained on the basis of charge-separated intermediates. As an extension of the work reported by Liotta,[16b] we find that diethyl (trimethylsilyl)phosphite adds to cyclopentenone at room temperature in nitromethane to give the adduct in 54% isolated yield.



35

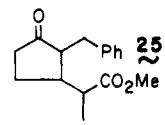
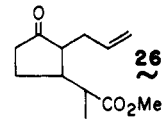
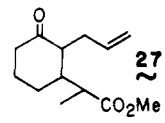
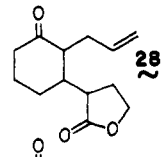
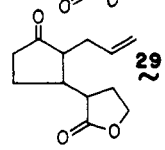
Alkylation of Enone–Silyl Ketene Acetal Adducts. The silyl enol ether adducts are useful synthetic intermediates. A scheme for the formation of two C–C bonds in one pot is illustrated by the benzylation and allylation of these adducts[4,10] (Table III). For example, benzylation of **4** in the presence of stoichiometric fluoride ion gives **25** as a 1:1 mixture of diastereomers. (The CH_3CH NMR signals in **25** appear as two overlapping doublets at δ 1.05 and 1.15 (J = 10 Hz) and the CO_2CH_3 as two singlets at δ 3.60 and 3.65). Allylation also gives a similar mixture **26**. There is no evidence for mixtures of cis and trans 2,3-isomers. The products are most likely trans since under the reaction conditions fluoride ion can act as a base to give the thermodynamically more stable trans isomer.[7b] In the alkylation of **6**, **12**, and **24**, the stereochemical outcome cannot be unambiguously ascertained because of the complex NMR spectra of the products.

Discussion

The Michael addition of silyl ketene acetals to enones proceeds if the acetals or enones are activated by TASF or Lewis acid, respectively. The evidence discussed above indicates that in the solvent-assisted additions, the silyl group of silyl ketene acetals **1** is not directly transferred to the adduct **2**. The significant solvent effects are consistent with the involvement of charge-separated intermediate **34** shown in Scheme II. The use of Me_3SiCl or other Lewis acids[2,14] extends the scope of this reaction to the additions of hindered ketene acetals.

(16) (a) Evans, D. A.; Hurst, K. M.; Takacs, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 3467. (b) Liotta, D.; Sunay, U.; Ginsberg, S. *J. Org. Chem.* **1982**, *47*, 2227.

Table III. Fluoride-Assisted Alkylations of Ketene Silyl Acetal–Enone Adducts

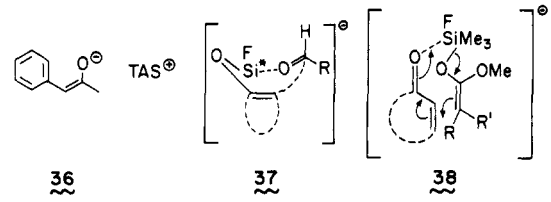
entry	adduct	alkylating agent	products (yield, %)
1	**4**	BENZYL BROMIDE	 (29)
2	**4**	ALLYL BROMIDE	 (25)
3	**6**	ALLYL BROMIDE	 (19)
4	**12**	ALLYL BROMIDE	 (29)
5	**24**	ALLYL BROMIDE	 (27)

The TASF-promoted addition is versatile and efficient. There are noteworthy reactivity differences, however, between the carbon nucleophiles generated from the combination of TASF–silyl enol ethers and the classical lithium enolate anions. In the former, while the nucleophilicity of the silyl enol ethers is enhanced, the basicity is not significantly increased. This difference proves to be advantageous for the conjugate addition of ketene trimethylsilyl acetals to α,β-unsaturated carbonyl compounds. Exceptionally good 1,4 addition under catalysis of TASF is observed without any complication from 1,2 additions, proton transfers, or undesired condensation reactions that usually plague metal enolate Michael additions.

Mechanistically, the TASF-catalyzed Michael addition shares basic features with the similarly catalyzed addition of silyl enol ethers to aldehydes.[5a,9,11] In the latter, it has been postulated that the initially formed TAS salt of "naked" enolate adds to aldehyde and the generated aldol anion is trapped by the in situ generated Me_3SiF. The high erythro selectivity observed irrespective of the geometry of the starting silyl enol ether has been presented as supportive evidence. Notably, however, the naked enolate **36** failed to give adducts in the absence of Me_3SiF.[12]

Relating the stereochemical outcome of a reaction to a model transition state is a heuristic exercise, especially so in this case since it has been shown that even in chelating metal systems like Zr,[13a] Sn,[13b] and Ti[13c] erythro selectivity predominates. Conformational preferences of the intermediates in these cases have been helpful to some extent in explaining the origin of this selectivity. In this context, the possibility of a hypervalent silicon intermediate such as **37** cannot be ruled out, as long as the geometric and electronic preferences of such an intermediate remain unknown. The intramolecular migration of silicon from one oxygen to the other within its coordination sphere could yield the product. Indeed, intermediacy of a hypervalent silicon was mentioned in an earlier paper.[9a]

In the TASF-catalyzed Michael reaction to enones reported in this paper, we have not been able to conclusively



36 37 38

Si* ≡ Me_3Si

demonstrate the nature (inter- vs. intramolecular) of silyl group transfer because, in the presence of TASF, the silyl group exchange between **1c** and **21** is very facile and proceeds at a rate comparable to or faster than their addition to cyclopentenone and methyl vinyl ketone. It should be mentioned, however, in the related reactions with α,β-unsaturated esters at low temperatures to form polymers, we have conclusively shown[14] that the silyl group of the silyl ketene acetal initiator does not reversibly dissociate. On the basis of similar crossover experiments, we have proposed an intramolecular silyl group transfer mechanism (Scheme III) involving hexacoordinate silicon species similar to **38** for the acrylate polymerization reactions and termed it "group-transfer polymerization" (GTP). Further studies on the mechanism of this Michael reaction and GTP will be discussed in future papers.

Experimental Section

Infrared spectra were determined on a Perkin-Elmer Model 21 double-beam Acculab 8 or a Nicolet Model 7199FT spectrometer. UV spectra were recorded on a Cary 17 spectrophotometer. NMR spectra were obtained on a Varian EM-390 or IBMNR80 or a Nicolet 360WB spectrometer, and chemical shifts are reported from tetramethylsilane and were recorded in $CDCl_3$ solutions unless otherwise indicated. Gas chromatography was done on a Hewlett-Packard 5710A model. Unless otherwise specified a glass column 6 ft × $^1/_8$ in. containing 3% SP2100 on Supelcoport 60/80 support was used with temperature programming.

All solvents were purified by standard procedures and were freshly distilled. Nitromethane was distilled from P_2O_5 and stored over 3-Å molecular sieves. Acetonitrile was refluxed with calcium hydride and was distilled fresh for each reaction.

Trimethylsilyl Ketene Acetals. These compounds were prepared by minor modification of standard procedures reported earlier.[17] The preparation of (*E*)-1-methoxy-1-(trimethylsiloxy)propene (**1a**) is illustrative.

A 1-L three-necked flask fitted with a thermometer well, addition funnel, and a serum stopper was charged with 70.08 mL (0.5 M) of diisopropylamine and 100 mL of anhydrous freshly distilled THF. The mixture was cooled to −20 °C, and 325 mL of 1.6 M *n*-BuLi solution in hexane was added from the dropping funnel at such a rate that the temperature of the mixture did not go above 0 °C. The mixture was further stirred for 10 min and subsequently cooled to −78 °C (inside temperature). From a dropping funnel 48.15 mL (0.5 M) of methyl propionate was added in 22 min. The last traces were washed down with 10 mL of THF. The mixture was stirred for 3 h, and then 70 mL of trimethylsilyl chloride (freshly distilled and stored over activated molecular sieve, 4Å) was added in 60 min. The cold bath and the reaction mixture were warmed to room temperature overnight (~18 h). The precipitated lithium chloride was filtered off by using a nitrogen pressure funnel. Excess THF, amine, and chlorotrimethylsilane are removed on the pump with rigorous exclusion of moisture, and the product was distilled under vacuum by using an efficient spinning band distillation column: bp 47–50 °C (26 mm); yield 27.84 g (35%); ^{1}H NMR δ 0.15 (s, 9 H), 1.35 (d, J = 6 Hz, 3 H), 3.40 (s, 3 H), 3.60 (q, J = 6 Hz, 1 H).

(17) (a) Ainsworth, C.; Chen, F.; Kuo, Y.-N. *J. Organomet. Chem.* **1972**, *46*, 59. (b) Ainsworth, C.; Kuo, Y.-N. *Ibid.* **1972**, *46*, 73.

1-Methoxy-1-(trimethylsiloxy)-2-methylpropene (**1b**), 2-(trimethylsiloxy)-4,5-dihydrofuran (**1c**), 1-methoxy-1-(triethylsiloxy)propene (**21**) were all prepared[17] by identical procedure. Ethyl (trimethylsilyl)acetate (**16**) is commercially available.

Fluoride-Catalyzed Additions. Fluoride-Catalyzed Addition of 1a to Cyclopentenone. To 106 mg (0.39 mmol) of TASF suspended in 15 mL of anhydrous THF was added 0.84 mL (10 mmol) of cyclopentenone and 1.93 mL (10 mmol) of **1a** dissolved in 10 mL of THF below −70 °C. After the addition had been completed (~12 min), 100 μL of acetic acid was added at −78 °C and the mixture was warmed to room temperature. The solvent was removed on the pump with rigorous exclusion of moisture; yield 2.20 g (91%). ^{1}H NMR and GC confirmed the structure as a diastereomeric (1:1) mixture of products **4** indistinguishable from that obtained via the thermal addition (vide infra):[7a] ^{1}H NMR (360 MHz) δ 0.15 (2s, separated by 5 Hz, 9 H), 1.05 (2d, J = 6 Hz, 3 H, separated by 4 Hz), 1.50 (m, 1 H), 1.90 (m, 1 H), 2.10–2.40 (m, 3 H), 2.90 (m, 1 H), 3.60 (2s, 3 H, separated by 1 Hz), 4.45 (m, 0.5 H), 4.55 (m, 0.5 H).

Hydrolysis of the adduct (see below for procedure) **4** yielded the keto ester **5** in 82% yield: IR (neat) 1738 cm^{-1}; ^{1}H NMR δ 1.20 (2d, J = 3 Hz, 3 H, diastereomeric CH_3's), 1.35–2.70 (m, br, 8 H), 3.60–3.70 (2s, diastereomeric OCH_3's, 3 H); HRMS m/e 170.0937 (M^+; calcd for $C_9H_{14}O_3$ 170.0940).

Fluoride-Catalyzed Addition of 1a to Cyclohexenone. Similar procedure (procedure A) as in the above experiment yielded 94% of the adduct **6**, whose structure was confirmed by comparison of physical properties with those of an authentic sample (vide infra).[7]

In an alternate procedure (procedure B), a homogeneous TASF solution in acetonitrile was used as catalyst. In a three-necked flask fitted with addition funnel, thermometer, and stirrer 0.400 g (1.45 mmol) of TASF, 5 mL of acetonitrile, and 20 mL of THF were charged, and at −78 °C, a mixture of 3.88 mL (21 mmol) of (**1a**) and 1.94 mL (20 mmol) of cyclohexenone in 10 mL of THF was added while the temperature was maintained below −70 °C (~30 min). After being stirred for 5 min at −78 °C, the cold reaction mixture was added to 150 mL of hexane and 30 mL of water. The aqueous layer was further extracted with hexane. The combined hexane extracts were washed with saturated sodium chloride, dried, concentrated, and Kugelrohr distilled to give 3.84 g (75%) of the adduct **6**.[7]

This product was hydrolyzed by stirring with silica gel impregnated with 6% oxalic acid solution in methylene chloride (see below). Distillation yielded **7** (78%) identified by comparison of its properties with those of an authentic sample prepared by an alternate procedure (vide infra): IR (neat) 1740, 1715 cm^{-1}; ^{1}H NMR δ 1.13–1.23 (2d, J = 2 Hz, diastereomeric CH_3's, 3 H), 1.35–2.67 (m, 10 H), 3.70 (s, 3 H); HRMS m/e 184.1095 (M^+; calcd for $C_{10}H_{16}O_3$ 184.1099).

General Procedure for Hydrolysis of the Primary Adducts 2. A 10-mmol solution of the adduct in 25 mL of methylene chloride was stirred with 10 g of silica gel impregnated with 1 mL of 6% oxalic acid. The reaction was followed by GC for the disappearance of starting material. Typically after 30 min to 1 h, the silica was filtered off and washed with 5% methanol and methylene chloride, and the product was isolated by concentration and Kugelrohr distillation. The following compounds were prepared by this procedure from the appropriate adducts (yields (%) are given in parentheses): **9** (75), **11** (53), **13** (58), **15** (74), **19** (85), and **20** (87).

Addition of 1b to Cyclopentenone. The general procedure B outlined earlier yielded 3.15 g (>95% pure by GC, 61% yield) of **8** from 1.70 mL (20 mmol) of cyclopentenone and 4.18 mL (21 mmol) of **1b** at −78 °C under catalysis of 0.248 g (0.91 mmol) of TASF; ^{1}H NMR (360 MHz) δ 0.12 (s, 9 H), 1.00 (2s, separated by 9 Hz, 6 H), 1.45 (m, 1 H), 1.80 (m, 1 H), 2.13 (m, 2 H), 2.90 (m, 1 H), 3.55 (s, 3 H), 4.40 (m, 1 H). The hydrolysis of the crude product followed by distillation yielded 1.70 g (75%) of **9**: IR (neat) 2980, 2960, 2930, 2900, 1740, 1155 cm^{-1}; ^{1}H NMR δ 1.20 (s, 6 H), 1.40–3.05 (m, 7 H), 3.65 (s, 3 H); HRMS m/e 125.0964 ($M^+ - C_2H_3O_2$; calcd for $C_8H_{13}O$ 125.0966).

Addition of 1b to Cyclohexenone. To a solution of 0.400 g (1.45 mmol) of TASF in 5 mL of acetonitrile and 30 mL of THF was added 1.94 mL (20 mmol) of cyclohexenone and 4.18 mL (21 mmol) of **1b** in 15 mL of THF at a rate so as to maintain tem-

perature below −70 °C (~30 min). After being stirred for 30 min, the reaction mixture was added to 150 mL of hexane and 40 mL of water. The organic layer was separated, and the aqueous layer was further extracted with hexane (50 mL × 2). The combined organic layers were washed and dried, and then the solvents were removed to get 3.499 g (65%) of **10**: IR (neat) 1740, 1720, 1665 cm^{-1}; ^1H NMR δ 0.10 (s, 9 H), 1.02 (s, 3 H), 1.04 (s, 3 H), 1.20–2.40 (m, 6 H), 2.46 (m, 1 H), 3.60 (s, 3 H), 4.60 (s, 1 H). Compound **10** was hydrolyzed by oxalic acid impregnated silica in methylene chloride. The product was distilled out to get 2.10 g (53%) of **11** (>95% pure by GC): IR (neat) 2750, 2950, 1730, 1715, 1135 cm^{-1}; ^1H NMR δ 1.10 (s, 6 H), 1.30–2.50 (m, 9 H), 3.75 (s, 3 H). At 360-MHz the signal at δ 1.10 resolves into two peaks of equal intensity (diastereotopic CH_3's): HRMS *m/e* 198.1237 (M^+; calcd for $C_{11}H_{18}O_3$ 198.1256), 139.1116 ($M^+ - C_2H_3O_2$; calcd 139.1123).

Addition of 16 to Cyclohexenone. With the general procedure B **18** and **20** were prepared in 62% and 87% (sublimed) yields, respectively. **18**: IR (neat) 1740, 1665 cm^{-1}; ^1H NMR δ 0.05 (s, 9 H), 1.15 (t, J = 8 Hz, 3 H), 1.40–2.00 (m, 6 H), 2.15 (d, J = 8 Hz, 2 H), 2.55 (m, 1 H), 4.00 (q, J = 8 Hz, 2 H), 4.65 (m, 1 H). **20**: IR (neat) 2970, 2930, 2860, 1730, 1710, 1155 cm^{-1}; ^1H NMR (360 MHz) δ 1.25 (t, J = 8 Hz, 3 H), 1.45 (m, 1 H), 1.70 (m, 1 H), 1.90–2.50 (m, 9 H), 4.12 (q, J = 8 Hz, 2 H); HRMS *m/e* 184.1100 (M^+; calcd for $C_{10}H_{16}O_3$ 184.1099), 155.0728 ($M^+ - C_2H_4$; calcd 155.0747), 139.0756 ($M^+ - C_2H_5O$; calcd 139.0759).

Addition of 16 to Cyclopentenone. The adducts **17** and **19** were prepared by general procedure B in 90% and 85% yields, respectively. **19**: IR (neat) 2970, 2950, 1745, 1145 cm^{-1}; ^1H NMR δ 1.20 (t, J = 6.7 Hz, 3 H), 1.40–2.80 (m, 9 H), 4.10 (q, J = 6.7 Hz, 2 H); HRMS *m/e* 120.0935 (M^+; calcd for $C_9H_{14}O_3$ 120.0943), 141.0547 ($M^+ - C_2H_5$; calcd 141.0552).

Addition of 2-(Trimethylsiloxy)-4,5-dihydrofuran (1c) to Methyl Vinyl Ketone. With procedure A the adduct(s) **14** was (were) prepared and further hydrolyzed to **15** in 74% yield. Purification was accomplished by Kugelrohr distillation (50 °C (0.02 mm)). **15**: ^1H NMR δ 1.30–2.55 (m, 5 H), 2.15 (s, 3 H), 2.65 (t, J = 8 Hz, 2 H), 4.10–4.40 (m, 2 H); HRMS *m/e* 156.0790 (M^+; calcd for $C_{10}H_{12}O_3$ 156.0790); anal. C, H. The NMR spectrum of **14** showed inter alia two singlets at δ 1.60 and 1.70 presumably arising from *E* and *Z* isomers.

Addition of 2-(Trimethylsiloxy)-4,5-dihydrofuran (1c) to Cyclohexenone. To 0.130 g (0.47 mmol) of TASF in 10 mL of anhydrous THF under nitrogen was added a mixture of 0.60 mL (3.58 mmol) of **1c** and 0.35 mL (3.63 mmol) of cyclohexenone in 2 mL of THF at −78 °C. The mixture was warmed to −40 °C and then added to excess hexane and water. The hexane layer was washed with water, and the intermediate **12** was isolated by removal of solvent. The hydrolysis of **12** was done as described earlier to give 0.38 g (58%) of the keto lactone **13**: IR (neat) 1775, 1720 cm^{-1}; ^1H NMR δ 1.20–2.80 (m, br, 12 H), 4.00–4.40 (m, 2 H); HRMS *m/e* 182.0952 (M^+; calcd for $C_{10}H_{14}O_3$ 182.0942).

Thermal Additions. General Procedure. A mixture of the enone and 5–10 mol % excess of ketene trialkylsilyl acetal in freshly distilled nitromethane was stirred at room temperature. The reaction was followed by GC (3% SP2100 on Supelcoport, 6 ft × $^1/_8$ in. glass column). Typically after 3–4 h the reaction was nearly complete. The stirring was continued overnight (~16–18 h), and solvent and excess reagents were removed on the pump with rigorous exclusion of moisture to get the adducts. The results are tabulated in Table II. A typical procedure follows.

Thermal Addition of 1c to Cyclopentenone. A mixture of 3.80 mL (45.0 mmol) of cyclopentenone and 9.21 mL (55.0 mmol) of **1c** in 10 mL of nitromethane was stirred at room temperature. The solvent and low boiling components were removed, and the product **24** was distilled on Kugelrohr, 110–118 °C (0.065 mm); yield 5.50 g (48%). The actual yield was nearly quantitative before distillation (>95% pure as determined by GC and NMR). Deterioration occurred during distillation: ^1H NMR (360 MHz) δ 0.15 (2s, separated by 1 Hz, 9 H), 1.45 (m, 0.5 H), 1.57 (m, 0.5 H), 1.80–2.60 (m, 6 H), 2.97 (m, 0.5 H), 3.10 (m, 0.5 H), 4.05–4.15 (m, 1 H), 4.20–4.27 (m, 1 H), 4.33 (s, br, 0.5 H), 4.68 (s, br, 0.5 H). The two peaks for $Si(CH_3)_3$ and olefinic proton indicate a diastereomeric mixture (1:1).

Hydrolysis of **24** on acidic silica gave 73% (isolated) yield of the keto lactone: bp 105 °C (0.038 mm); IR (neat) 1765, 1740 cm^{-1}; ^1H NMR δ 1.40–3.00 (m, br, 10 H), 4.10–4.60 (m, br, 2 H); HRMS *m/e* 168.0785 (M^+; calcd for $C_9H_{12}O_3$ 168.0786); anal. C, H.

Other Adducts Prepared by This Procedure. 4: 82%. **6** (58%): IR 1735, 1665 cm^{-1}; ^1H NMR δ 0.15 (s, 9 H), 1.00 (d, J = 1 Hz, 1.5 H), 1.10 (s, J = 1 Hz, 1.5 H), 1.10–2.50 (m, br, 8 H), 3.63 (2s, 3 H), 4.60 (s, br, 0.5 H), 4.76 (s, br, 0.5 H); δ 4.60 and 4.76 are diastereomeric olefinic protons. **12** (46%): ^1H NMR δ 0.15 (s, 9 H), 1.50–3.00 (m, br, 10 H), 4.20–4.60 (m, br, 2 H), 4.70 (s, br, 0.5 H), 5.15 (s, br, 0.5 H); the last two are diastereomeric olefinic protons. **22** (67%): IR (neat) 1740, 1670 cm^{-1}; ^1H NMR δ 0.03 (s, 9 H), 1.00 (d, J = 5 Hz, 3 H), 1.56 (s, br, 3 H), 1.83–2.50 (m, br, 3 H), 3.50 (s, br, 3 H), 4.13–4.67 (br m, 1 H); HRMS *m/e* 230.1344 (M^+; calcd for $C_{11}H_{22}O_3Si$ 230.1338), 215.1116 ($M^+ - CH_3$; calcd 215.1104), 199.1141 ($M^+ - OCH_3$; calcd 199.1154).

Hydrolysis of 3.69 g of **22** on oxalic acid impregnated silica gave the expected keto ester (1.48 g): IR (neat) 1735, 1720 cm^{-1}; HRMS *m/e* 159.1003 (M^+ + 1; calcd for $C_8H_{15}O_3$ 159.1021), 127.0751 ($M^+ - OCH_3$; calcd 127.0759).

23 (92%): IR (neat) 1740, 1645 cm^{-1}; ^1H NMR (360 MHz) δ 0.65 (m, 6 H), 0.92 (two sets of t, J = 8 Hz, 9 H), 1.05 (two sets of doublets, J = 7 Hz, 3 H), 1.30 (m, 1 H), 1.75 (m, 1 H), 1.95–2.15 (m, 4 H), 3.61 (s, 3 H), 4.45 (q, J = 2 Hz, 0.5 H), 4.57 (q, J = 2 Hz, 0.5 H); HRMS *m/e* 284.1787 (M^+; calcd for $C_{15}H_{28}O_3Si$ 284.1807), 197.1367 ($M^+ - C_4H_2O_2$; calcd 197.1361).

Attempted Addition of 1b to Cyclopentenone. A mixture of 0.50 mL (5.96 mmol) of cyclopentenone and 1.10 mL (5.52 mmol) of **1b** was stirred at room temperature for 17 h and subsequently maintained to 80 °C for 18 h. Very little of the expected product **8** (<5%) was observed by GC.

The same result was obtained by doing the reaction under identical conditions in acetonitrile.

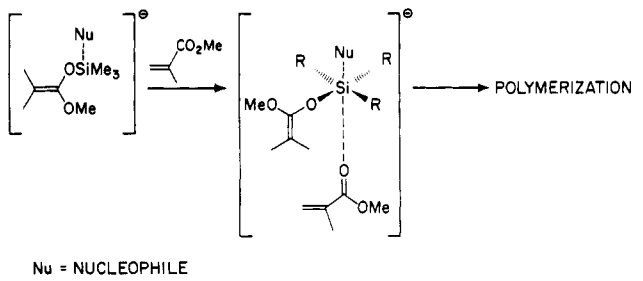
Addition of 21 to Cyclopentenone in the Presence of Me_3SiCl. To a mixture of 0.42 mL of cyclopentenone (5 mmol) and 1.27 mL (10 mmol) of trimethylsilyl chloride in 5 mL of acetonitrile was added 1.13 mL (5.10 mmol) of **21**. An exothermic (23 → 39.7 °C) reaction took place with complete disappearance of **21** in 1 h. The mixture was stirred for 24 h, and the low boiling components were removed on the pump. The ratio of products **4** and **23** (1.90 g, 67%) was determined by GC, and the structures were confirmed by comparison of GC retention times with those of authentic samples and GC mass spectrometry: **4** (19%) and **23** (81%).

Addition of 1b to Cyclopentenone in the Presence of Me_3SiCl. A mixture of 0.41 mL (5 mmol) of cyclopentenone, 1.19 mL (6 mmol) of **1b**, and 1.27 mL (10 mmol) of Me_3SiCl was dissolved in 6 mL of dry nitromethane, and the mixture was stirred at room temperature until the starting materials disappeared (6 h). The solvent and low boiling components were removed on the high vacuum pump, and the product **8** was analyzed by GC and NMR. The crude material was >95% pure; yield 0.857 g (67%). Acetonitrile after 24 h gave only 28% yield. Methylene chloride and THF were also unsatisfactory solvents for this reaction.

Additions of Diethyl Trimethylsilyl Phosphite. A mixture of 0.84 mL (10 mmol) of cyclopentenone and 2.16 mL (9.50 mmol) of diethyl trimethylsilyl phosphite in 5 mL of freshly distilled (P_2O_5) nitromethane was stirred at room temperature for 134 h. The low boiling components were removed on a high vacuum pump. Kugelrohr distillation yielded 1.50 g (54%) of **35** (96% pure by GC): IR (neat) 3080, 2980, 2960, 2850, 1640, 1255, 1060, 1030, 960, 850, 755 cm^{-1}; ^1H NMR δ 0.06 (s, 9 H), 1.05–1.30 (2t, br, J = 7 Hz, 6 H), 1.75–2.40 (m, 4 H), 2.50–3.00 (m, br, 1 H), 3.45–3.75 (m, superimposed on t, J = 7 Hz, 5 H); HRMS *m/e* 292.1252 (M^+; calcd for $C_{12}H_{25}O_4PSi$ 292.1259).

Benzylation of 4. A solution of 1.225 g (5 mmol) of the adduct **4** in 10 mL of THF was cooled to −78 °C. Benzyl bromide (0.78 mL, 6.6 mmol) was added followed by 1.78 g (6.5 mmol) of TASF in 10 mL of pyridine and THF (1:1). The reaction continued for 2 h at −78 °C. The mixture was warmed to room temperature, and excess hexane was added. The precipitated TASBr was filtered off, and the organic layer was washed with 40 mL of 1 N HCl. The organic layer was separated, and the aqueous layer was further extracted with ether (50 mL × 3). The combined organic extracts were washed with 1 N HCl (~30 mL), saturated sodium bicarbonate (~30 mL), and water (~30 mL). Dried ether layer was concentrated, and the products were separated by chromatography on silica gel with the ethyl acetate/hexane solvent

Scheme III



Nu = NUCLEOPHILE

system. Two products were isolated and identified. The first component (0.378 g, 29%) was the benzylated ester **25**: IR (neat) 1738 cm^{-1}; ^1H NMR δ 1.05 (d, J = 10 Hz), 1.15 (d, J = 10 Hz), together 3 H, 1.30–2.75 (m, br, 7 H), 2.90 (m, br, 2 H), 3.65 (2s, separated by 3 Hz, diastereomeric, 3 H), 7.20 (s, br, 5 H); HRMS m/e 260.1412, (M^+; calcd for $C_{16}H_{20}O_3$ 260.1407).

The second component (0.160, 19%) was identified as the hydrolysis product **5** of the intermediate silyl enol ether by comparison of spectral properties with those of an authentic sample prepared by acid hydrolysis of **4**.

Allylation of 4. A mixture of 1.22 g (5 mmol) of silyl enol ether **4** and 0.838 g (6.9 mmol) of allyl bromide in THF was added to a solution of 1.38 g (5 mmol) TASF in 40 mL of 1:1 pyridine and THF at −78 °C. The mixture was stirred for 105 min and then warmed to room temperature. Excess (~80 mL) hexane was added, and the precipitated TASBr was filtered off. The solid was washed with additional 40 mL of hexane. HCl (1 N, 30 mL) was added and the organic layer extracted with ether. Drying, concentration, and chromatography (silica, 30% ether/hexanes) yielded the allylated product **26** (0.264 g, 25%) in addition to the hydrolyzed product **5** (0.240 g, 29%) of the silyl enol ether that was identified by comparison of the spectral properties with those of an authentic sample prepared by an alternate procedure. **26**: IR (neat) 1738 cm^{-1}; ^1H NMR δ 1.15 (d, J = 5 Hz), 1.25 (d, J = 5 Hz, diastereomeric $CH_3CH{\cdot}CO_2Me$, δ 1.15 and 1.25 together 3 H), 1.37–2.87 (m, 9 H), 3.68 (two singlets diastereomeric CO_2CH_3, 3 H), 4.95–6.01 (m, 3 H); HRMS m/e 210.1248 (M^+; calcd for $C_{12}H_{18}O_3$ 210.1256).

Allylation of Silyl Enol Ether 6. A 100-mL flask was charged with 1.85 g (7.25 mmol) of silyl enol ether and 0.65 mL (1 equiv) of allyl bromide in 20 mL of THF. The mixture was cooled to −78 °C, and 1.90 g (6.91 mmol) of TASF dissolved in 5 mL of acetonitrile and 5 mL of THF was added. Stirring was continued for 20 h and then warmed to room temperature (~10 min). Hexane (100 mL) and 30 mL of water were added. Organic layer was separated and extraction of the aqueous layer with additional ether (2 × 50 mL) and isolation of product by standard techniques gave a mixture that was separated on a silica column with 25% ethyl acetate/hexane as solvent. The first fraction was identified as the allylated product **27** (19%) by the following spectral data: IR (neat) 1745, 1715 cm^{-1}; ^1H NMR δ 1.13 (d, J = 7Hz), 1.20 (d, J = 7 Hz, together 3 H), 1.33–3.00 (m, br, 11 H), 3.70 (2s, separated by ~1 Hz, diastereomeric CH_3's), 4.90–5920 (m, 2 H), 5.50–6.13 (m, 1 H); HRMS m/e 224.1411 (M^+; calcd for $C_{13}H_{20}O_3$ 224.1412). The second component was identified as the hydrolysis product **7** prepared earlier by acid treatment of **6**.

Allylation of Adduct 12. A mixture of 3.55 g (14 mmol) of **12** and 1.27 mL (14.70 mmol) of allyl bromide in 20 mL of THF was cooled to −78 °C. From a dropping funnel a solution of 3.848 g (14 mmol) of TASF in 10 mL of CH_3CN was added dropwise. The mixture was stirred at −78 °C for 22 h. Water (40 mL) and hexane (100 mL) were added, and the organic layer was separated. The aqueous layer was extracted with ether (50 mL × 2), and the combined organic layer was dried and concentrated. Chromatography on silica (ether) yielded the allylated ketone as a mixture of diastereomers of **28** (29%) that was only partly separated. The component that was separated cleanly showed the following spectral characteristics: IR (neat) 1770, 1715 cm^{-1}; ^1H NMR δ 1.30–3.05 (m, 13 H), 4.05–4.50 (m, 2 H), 4.80–5.40 (m, 2 H), 5.50–6.05 (m, 1 H); HRMS m/e 222.1238 (M^+; calcd for $C_{13}H_{18}O_3$ 222.1256). The second fraction, which was isolated only as a mixture of the first component and a second isomer, had very similar spectral behavior.

Allylation of Adduct 24. To a mixture of 1.60 g (6.7 mmol) of silyl ether **24** and 0.605 mL (7 mmol) of allyl bromide in ~10 mL of THF was added a solution of 1.84 g (6.7 mmol) of TASF in acetonitrile at −78 °C. The mixture was stirred for 20 h at −78 °C, warmed to room temperature, and worked up. Chromatography on silica (ether) yielded the desired product(s) **29** (27%) (IR (neat) 1780, 1750 cm^{-1}; ^1H NMR δ 1.10–3.20 (m, br, 11 H), 4.10–4.60 (m, 2 H), 4.85–5.30 (m, 2 H), 5.40–6.00 (m, 1 H); HRMS m/e 208.1100 (M^+; calcd for $C_{12}H_{16}O_3$ 28.1099), in addition to the simple hydrolysis product.

Attempted Silyl Exchange between 1c and 21. A mixture of 0.17 mL (1.00 mmol) of **1c** and 0.24 mL (1.00 mmol) of **21** in 1 mL of nitromethane was stirred at room temperature and the reaction was followed by GC and NMR. There was no sign of the appearance of crossover products over 24 h.

In acetonitrile the same results were also observed. A CD_3CN solution of **1c** and **21** remains unchanged over several weeks as determined by 360-MHz NMR spectrum and GC analysis.

Solvent-Assisted Reaction of Cyclopentenone with 1c and 21. A mixture of 0.84 mL (10 mmol) of cyclopentenone, 1.19 mL (5 mmol) of **21**, and 0.68 mL (5 mmol) of **1c** in 5 mL of nitromethane was stirred at room temperature. An exothermic reaction ensued upon mixing. GC indicated complete disappearance of **21** after 35 min. After 2 h the solvent was removed to get an exceptionally clean mixture of 2.20 g (89%) of products that were analyzed by GC (3% SP2100 on 80/100 Supelcoport 6 ft × $^1/_8$ in. glass column; programmed run 80 °C/4 min to 240 °C increased at a rate of 16 °C/min) and GC–HRMS.

In acetonitrile, the reaction was much slower. Over 24 h the yield was only 62%. A random distribution products were obtained in both cases: in acetonitrile, for example, **4** (18%), **24** (32%), **23** (29%), and **30** (21%).

Solvent-Assisted Reaction of Methyl Vinyl Ketone with 1c and 21. A mixture of 0.82 mL (10 mmol) of methyl vinyl ketone and 0.68 mL (4 mmole of **1c** and 1.19 mL (5 mmol) of **21** was stirred at room temperature in nitromethane for 24 h. The reaction was followed by GC using 3% SP2100 column. The product structures were confirmed by comparison of retention times and GC–MS with those of authentic samples: **14** (21%), **31** (46%), **22** (23%), and **32** (10%). A comparable reaction in acetonitrile required 96 h at room temperature.

Solvent-Assisted Reaction of Cyclopentenone with 1b in the Presence of 21. A mixture of 1.99 mL (10 mmol) of **1b**, 1.19 mL (5 mmol) of **21**, and 0.83 mL (10 mmol) of cyclopentenone in 5 mL of acetonitrile was stirred at room temperature. After the exothermic reaction subsided, the mixture was stirred for 20 h. The low boiling components were removed on the pump to get 1.01 g (36% with respect to cyclopentenone) of an oil that was analyzed by GC and GC–HRMS for the composition of the four products: **4** (12%), **8** (13%), **23** (39%), and **33** (36%).

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Registry No. **1a**, 72658-09-4; **1b**, 31469-15-5; **1c**, 51425-66-2; **4** (isomer 1), 89597-23-9; **4** (isomer 2), 89597-42-2; **5** (isomer 1), 84307-67-5; **5** (isomer 2), 84307-68-6; **6** (isomer 1), 89597-24-0; **6** (isomer 2), 89597-43-3; **7** (isomer 1), 89597-25-1; **7** (isomer 2), 89597-44-4; **8**, 89597-26-2; **9**, 89597-27-3; **10**, 89597-28-4; **11**, 58649-09-5; **12** (isomer 1), 89597-29-5; **12** (isomer 2), 89597-47-7; **13** (isomer 1), 89597-30-8; **13** (isomer 2), 89597-45-5; **15**, 27927-78-2; **16**, 4071-88-9; **17**, 89597-31-9; **18**, 89597-32-0; **19**, 62457-60-7; **20**, 66427-26-7; **21**, 89597-33-1; *trans*-**22**, 89597-34-2; *cis*-**22**, 89597-49-9; **23** (isomer 1), 89597-35-3; **23** (isomer 2), 89689-32-7; **24** (isomer 1), 89597-36-4; **24** (isomer 2), 89597-46-6; **25** (isomer 1), 89597-37-5; **25** (isomer 2), 89673-89-2; **26** (isomer 1), 89597-38-6; **26** (isomer 2), 89673-90-5; **27** (isomer 1), 89597-39-7; **27** (isomer 2), 89673-91-6; **28** (isomer 1), 89597-40-0; **28** (isomer 2), 89673-92-7; **29** (isomer 1), 89597-41-1; **29** (isomer 2), 89673-93-8; **30**, 89597-50-2; **31**, 89597-51-3; **32**, 89597-52-4; **33**, 89597-53-5; **35**, 81435-28-1; $CH_3C(O)CH{=}CH_2$, 78-94-4; $CH_3CH{=}C(OSiMe_3)_2$, 31469-22-4; Me_3SiCl, 75-77-4; $PhCH_2Br$, 28807-97-8; TASF, 59201-86-4; 2-cyclopenten-1-one, 930-30-3; cyclohexenone, 25512-62-3; 1,1,4,4-tetramethyl-6-ethylidene-1,4-disila-5,7-dioxacycloheptane, 89597-48-8; methyl 2-methyl-5-oxohexanoate, 38872-30-9; diethyl trimethylsilyl phosphite, 13716-45-5; allyl bromide, 106-95-6.