bromides **36** and **37** are apparently unknown; however, procedures for the preparation of the corresponding iodides and chlorides have been reported that give isomeric mixtures.[15,16] A very recent report describes the first method where either of the chlorides corresponding to **36** or **37** can be made to predominate.[17] The selective preparation of the vinylstannane **28** is made possible by the trapping of the enolate generated by the conjugate addition of lithium dimethylcuprate to 2-methylcyclohexenone.[12] The 2-(trimethylstannyl)-1,3-cyclohexadiene **24** is accessible from the kinetic enolate of cyclohexenone, whereas, the preparation of the 1-(trimethylstannyl)-1,3-cyclohexadiene **31** is made possible by a procedure recently introduced by Krafft and Holton for the preparation of the thermodynamic enol derivatives of cyclohexenones.[18] The need for excess catalyst over the standard amount in some of the reactions in Table I can be obviated by addition of 5 mol % triphenylphosphine.

The cleavage of vinylstannanes with alkyllithiums is an often used method for the convenient generation of vinyllithiums.[6,7] Caution should be exercised in the synthetic applications of these transmetalations since they are equilibrium reactions[6] which may not be favorable in all cases nor may all electrophiles have favorable rate constants for reaction with the predominate species. For example, in an effort to prepare the cyclohexenyl chromium carbene complex **40**, a THF solution of the vinylstannane **12** that had been pretreated with 1 equiv of methyllithium was transferred to a solution of chromium hexacarbonyl. Upon methylation a 7.2/1.0 mixture of the methyl carbene complex **39** and the cyclohexenyl complex **40** was obtained (Scheme III). The same result was obtained by starting with cyclohexenyllithium and tetramethylstannane.[19] Thus, at least with chromium carbonyl as the electrophile, it is necessary to generate the vinyllithium from the corresponding halide which can be readily obtained from the triflate by quenching the coupling reaction with a halogen.

The palladium(0)-catalyzed coupling of enol triflates and hexamethyldistannane provides for a new synthesis of vinylstannanes and thus a new synthetic entry to vinyllithiums. The vinylstannanes can be regioselectively prepared from unsymmetrical ketones in two steps wherever the metal enolates of the ketones can be generated selectively.

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Supplementary Material Available: Experimental procedure for **26** and spectral data for compounds **10–23**, **25–34**, **36**, and **37** (7 pages). Ordering information is given on any current masthead page.

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[15] Chlorides: (a) Montgomery, L. K.; Applegate, L. E. *J. Am. Chem. Soc.* **1967**, *89*, 2952. (b) Mousseron, M.; Jacquier, R. *Bull. Soc. Chim. Fr.* **1950**, 648. Iodides: Bottini, A. T.; Corson, F. P.; Fritzgerald, K.; Frost, K. A., II. *Tetrahedron* **1972**, *28*, 4883.

[16] A selective preparation of 2-methyl-1-chlorocyclohexene has been described: Gassman, P. G.; Valcho, J. J.; Proehl, G. S.; Cooper, C. F. *J. Am. Chem. Soc.* **1980**, *102*, 6519.

[17] Hudrlik, P. F.; Kulkarni, A. K. *Tetrahedron* **1985**, *41*, 1179.

[18] Krafft, M. E.; Holton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 7619.

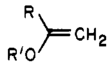
[19] The combined yield of **38** and **39** is 17% from both sides of the equilibrium. The reason for the low overall yield is not understood.

Stereoselection in the Michael Addition Reaction. 4. Diastereofacial Preferences in Lewis Acid Mediated Additions of Enolsilanes to Chiral Enones[1]

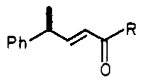
Summary: Chiral enones show good to excellent diastereofacial preference in their $TiCl_4$-mediated reactions with achiral and chiral enolsilanes; the method is shown to be useful for the preparation of acyclic 1,5-diketones and 1,5-keto acids having two or three stereocenters.

Sir: In a previous publication in this series,[2] we have reported that chiral aldehydes show high intrinsic diastereofacial preferences in their Lewis acid mediated reactions with enolsilanes and ketene acetals. Interestingly, these aldehydes show only modest diastereofacial preferences in their reactions with allylsilanes.[3] We have now extended our study to the reactions of the Lewis acid mediated reactions of chiral enones with enolsilanes and ketene acetals and report herein that good to excellent diastereofacial preferences are observed.

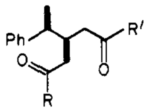
For our initial study, which addressed the question of diastereofacial preference of the enone only, the achiral enolsilanes **1–4** and chiral enones **5–7** were employed. Reactions were carried out by premixing the enone and titanium tetrachloride in methylene chloride at −78 °C. Excess enolsilane (1.3–2.9 equiv) was added over a period of 30 min, and the reaction was quenched after 1 h by the addition of aqueous potassium carbonate. Diastereomer ratios were obtained by capillary GLPC or proton NMR spectroscopy on the crude product mixture. In each case, the products were mixtures of two diastereomers (**8**/**9**, **10**/**11**, **12**/**13**, or **14**/**15**). Stereostructures were determined by ^1H NMR spectroscopy, using the relative chemical shifts of the R and R′ resonances, as has been discussed previously.[3,4] Results are shown in Table I.



1: R = *t*-Bu, R′ = Me_3Si
2: R = *t*-Bu, R′ = *t*-$BuMe_2Si$
3: R = Ph, R′ = Me_3Si
4: R = *t*-BuO, R′ = *t*-$BuMe_2Si$



5: R = Me
6: R = *t*-Bu
7: R = Ph



8: R = Me, R′ = *t*-Bu
9: R = *t*-Bu, R′ = Me
10: R = Me, R′ = Ph
11: R = Ph, R′ = Me
12: R = *t*-Bu, R′ = Ph
13: R = Ph, R′ = *t*-Bu
14: R = OH, R′ = *t*-Bu
15: R = *t*-Bu, R′ = OH

As shown in the table, diastereomer ratios are uniformly good, falling in the range from 8:1 to >30:1. In all cases the major isomer results from *ul* topicity (attack of enolsilane on the *re* face of the *S* enantiomer of the enone).[5,6]

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[1] Part 34 in the series "Acyclic Stereoselection". For part 33, see: Heathcock, C. H.; Finkelstein, B. E.; Aoki, T.; Poulter, C. D. *Science (Washington, D.C., 1883–)* **1985**, *229*, 862.

[2] Heathcock, C. H.; Flippin, L. A. *J. Am. Chem. Soc.*, **1983**, *105*, 1667.

[3] Heathcock, C. H.; Kikooka, S.-T.; Blumenkopf, T. A. *J. Org. Chem.* **1984**, *49*, 4214.

[4] Heathcock, C. H.; Lampe, J. *J. Org. Chem.* **1983**, *48*, 4330.

0022-3263/86/1951-0279$01.50/0

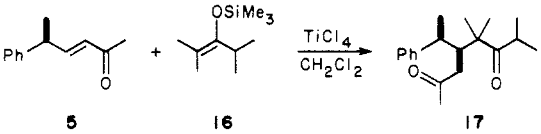
Table I. Stereochemistry of Addition of Enolsilanes to Enones

entry	enolsilane	enone	equiv of enolsilane	yield, %	products	diastereomer ratio
1	**1**	**5**	2.9	69	**8**,**9**	89:11
2	**2**	**5**	2.0	59	**5**,**9**	95:5
3	**3**	**5**	2.0	60	**10**,**11**	92:8
4	**3**	**6**	2.0	64	**12**,**13**	93:7
5	**1**	**7**	2.2	62	**13**,**12**	84:16
6	**2**	**7**	1.3	46	**13**,**12**	84:16
7	**4**	**6**	1.8	72	**14**,**15**[a]	97:3[b]

[a] The initial product is a mixture of *tert*-butyldimethylsilyl and *tert*-butyl esters (92%) and 1,2-addition product (8%); keto acids **14** and **15** were isolated after saponification. [b] Ratio given is for the 1,4-addition products.

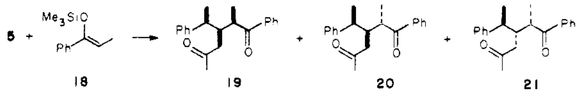
As was observed in the additions of achiral enolsilanes to chiral aldehydes,[2] (*tert*-butyldimethylsilyl)oxy compounds show somewhat better stereoselectivity than (trimethylsilyl)oxy compounds, presumably because they are more bulky and therefore discriminate more effectively between the diastereomeric transition states. Note that either diastereomer of the product dicarbonyl compounds may be obtained by an appropriate choice of substituents in the enone and enolsilane. For example, reaction of enol silane **3** with enone **6** gives predominantly (93%) dione **12**, while addition of enolsilane **2** to enone **7** provides mainly (84%) the diastereomeric dione **13**.

It has recently been shown that diastereofacial selectivity in the reactions of achiral enolates with chiral aldehydes is strongly dependent on the degree of substitution at the nucleophilic carbon.[7] The same trend is observed in the reactions currently under discussion; reaction of enone **5** with the fully substituted enolsilane **16** gives a single product, **17** (58% yield, eq 1).

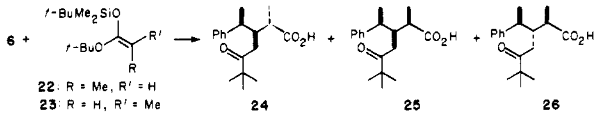


(1)

Since the Lewis acid mediated reactions of prochiral enones and prochiral enolsilanes often show excellent simple diastereoselection,[8] we also examined the reactions of chiral enones **5** and **6** with prochiral enolsilanes. In all cases studied, one of the four possible diastereomeric products greatly predominates. For example, reaction of enone **5** with **18**, the *Z* enolsilane from propiophenone, provides diones **19**–**21** (69% yield) in a ratio of 82:12:6 (eq 2). The major product of this mixture, **19**, was characterized by single-crystal X-ray analysis. Reaction of **6** with **22**, the *E* silyl ketene acetal from *tert*-butyl propionate, gives three products, **24**–**26**, in a ratio of 89:7:4 (62% yield), while **23**, the isomeric *Z* silyl ketene acetal, provides the same three keto acids in a ratio of 86:5:9 (79% yield, eq 3). The stereostructure of the major isomer, **24**, was vouchsafed by single-crystal X-ray analysis.



(2)



(3)

The results reported here provide further mechanistic information relative to the Mukaiyama–Michael reaction. In a previous communication,[8] we reported that simple diastereoselection is usually higher in the reactions of prochiral enones with ketene acetals than it is with enolsilanes. Furthermore, it was found that, to the extent that stereoselectivity is observed with enolsilanes, it is the product of *ul* topicity that is preferred (reaction of *si* face of the enone with *re* face of the enolsilane), while ketene acetals give largely the product of *lk* topicity.[5] The results were rationalized by hypothesizing that the ketene acetal reactions are under kinetic control and that the enolsilane reactions are under some degree of thermodynamic control, due to Michael reversion before loss of the silyl group from the oxygen atom of the new carbonyl group.[8] The results reported in this communication are difficult to reconcile with this mechanistic interpretation. If equilibration at the stage of the intermediate *O*-silyloxonium ion were playing an important role in the reaction, one might expect enolsilane **2** to show *lower selectivity* than **1**, since the *tert*-butyldimethylsilyl group should be lost less readily than the trimethylsilyl group. Furthermore, one might also expect that enolsilane **16** would show rather low stereoselectivity, since the presence of a quaternary center in the initial zwitterionic Michael adduct would be expected to foster reversion.

On the other hand, it might be that the initial zwitterionic products from reactions of unsubstituted enolsilanes **1**–**3** lack a suitable driving force for Michael reversion and that the reactions of these compounds are under effective kinetic control. With enolsilane **16** some Michael reversion may be occurring. However, if the diastereofacial selectivity with **16** is exceedingly high, as it is in analogous fully substituted lithium enolates,[7] a significant number of reversions may occur with no detectable effect on the diastereomer ratio.

Although a fully convincing mechanistic interpretation of the stereochemistry of the Mukaiyama–Michael reaction may still be lacking, the results reported herein should be of general synthetic utility for preparation of acyclic 1,5-diketones and 1,5-keto acids having two or three stereocenters.

Acknowledgment. This work was supported by a research grant from the United States Public Health Service (A115027).

Supplementary Material Available: A listing of the ^{13}C NMR chemical shifts of the products summarized in Table I and eq 1–3 (2 pages). See any current masthead page for ordering information.

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(5) For a definition of the *lk*, *ul* nomenclature for reaction topicity, see: Seebach, D.; Prelog, V. *Angew. Chem.* **1982**, *94*, 696.

(6) Because of the near symmetry in compounds **8**–**15**, the Seebach–Prelog technique for description of reaction topicity is especially valuable. For example, the reactions summarized in entries 4 and 5 of Table I give the same pair of products, with **12** being the major isomer in entry 4 and **13** being the major isomer in entry 5. It is obvious that qualitative stereochemical descriptors such as erythro/threo and syn/anti are highly ambiguous in this case. Furthermore, the *lk*,*ul* method can even be used to described the stereochemistry of the reaction of enolsilane **2** with enone **6**, a process clearly having two diastereomeric transition states, *both of which lead to the same product.*

(7) (a) Flippin, L. A.; Onan, K. D. *Tetrahedron Lett.* **1985**, *26*, 973. (b) Flippin, L. A.; Domboski, M. A. *Ibid.* **1985**, *26*, 2977. (c) Uenishi, J.; Tomazane, H.; Yamato, M. *J. Chem. Soc., Chem. Commun.* **1985**, 717.

(8) Heathcock, C. H.; Norman, M. H.; Uehling, D. E. *J. Am. Chem. Soc.* **1985**, *107*, 2797.