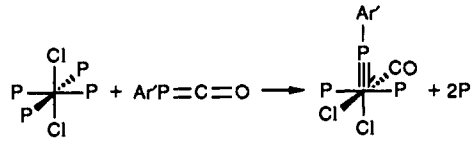
structure (**2b**) and a 1,2 P=C addition product on solely spectroscopic evidence.[9,10] An X-ray crystal structure of **4** was therefore undertaken.[11] The solid state of **4** (Figure 1) comprises isolated molecules with no short intermolecular contacts. The geometry at tungsten is octahedral, and the chloride and phosphine ligands adopt mutually cis and trans geometries, respectively.



P = $PMePh_2$; Ar' = 2,4,6-*t*-$Bu_3C_6H_2$

Ignoring the phosphine substituents, there is close to a mirror plane through the atoms W, Cl(1), Cl(2), C, O, and P(3). Although there is appreciable variation in the bond angles at tungsten, there is no evidence for distortion toward a bound η^2-OCPAr' form as evidenced by the following facts: (i) the P(3)-W-C angle is 90.1 (2)°, (ii) the W-C-O angle is essentially linear (177.9 (6))°, and (iii) the P(3)···C distance (2.93 Å) greatly exceeds the sum of covalent radii (1.83 Å). The phosphorus-tungsten distance (2.169 (1) Å) and C-P-W angle (168.2 (2)°) in **4** are particularly noteworthy. These data contrast with the analogous parameters for $Mo(\eta\text{-}C_5H_5)_2(=PAr')$ (Mo-P 2.370 (2) Å and Mo-P-C 115.8 (2)°)[4] and clearly establish that **4** is a linear terminal phosphinidene complex. In fact, the phosphorus-tungsten distance is the shortest such distance we are aware of and is consistent with a triple-bond description, viz., W≡P. The triple bond designation also explains the relatively upfield ^{31}P chemical shift for **4** since it is well-known that the phosphorus atoms of phosphaalkynes (RC≡P) are more shielded than those of phosphaalkenes (R_2C=PR').[12]

The strong π-donor character of the phosphinidene moiety can be inferred from the observation that the CO stretching frequency for **4** is significantly less than those for sulfido or terminal imido complexes ($W(X)Cl_2(CO)(PMePh_2)_2$: X = S, ν_{CO} = 1986 cm^{-1}; X = NAr, ν_{CO} = 1964 cm^{-1}).[5b] Such a view is consistent with the observation that the W-Cl bond trans to the phosphinidene ligand is ~0.04 Å shorter than that trans to CO.

Compound **3** also reacts with Ar'P=C=NPh.[13] Initially a $^{31}P\{^1H\}$ NMR spectrum is observed that is very similar to that of **4** and thus indicative of the composition $WCl_2(CNPh)(PMePh_2)_2(=PAr')$ (**6**). However, **6** is not thermally stable and decomposes in a few hours at 25 °C.

The reactivity of **4** and the reactions of **3** with other group 15 multiply bonded compounds are under active investigation.

Acknowledgment. We are grateful to the National Science Foundation and the Robert A. Welch Foundation for financial support.

(9) $^{31}P\{^1H\}$ NMR (121.5 MHz, 295 K, 85% H_3PO_4 external standard): **4** (C_6D_6) $\delta_{phosphinidene}$ = 193.0, t, with ^{183}W satellites, $^2J_{PP}$ = 50.0 Hz, $^1J_{PW}$ = 649 Hz; $\delta_{phosphine}$ = -0.1, d, with ^{183}W satellites, $^2J_{PP}$ = 50.0 Hz, $^1J_{PW}$ = 253 Hz. $^{13}C\{^1H\}$ NMR (75.5 MHz, 295 K, TMS): **4** (THF) δ 16.2 (d of t, $^1J_{PC}$ = 15.0 Hz, $^3J_{PC}$ = 1.5 Hz, P-*Me*), 31.1 (q, J_{PC} = 9.5 Hz, para-C-*Me*$_3$), 33.1 (pseudo q, J_{PC} = 8.7 Hz, ortho-C-*Me*$_3$), 36.4 (s, para-*C*-Me_3), 38.3 (s, ortho-*C*-Me_3), 122.9-123.1 (m, para Ph), 128.4 (s, meta Ar'), 129.8-130.3 (m, meta Ph), 133.4-133.7 (m, ortho Ph), 138.8-140.3 (t, $^1J_{PC}$ = 20.5 Hz, ipso *C* (Ph)), 148.4 (d, $^1J_{PC}$ = 37.7 Hz, ipso *C*(Ar')), 154.9 (d, $^2J_{PC}$ = 4.2 Hz, ortho Ar'), 156.9 (s, para Ar'), 244.6 (d of t, J_{PC} = 25.5 Hz, J_{PC} = 6.4 Hz, CO).

(10) The highest *m/e* peak in the FAB-MS of **4** occurred at 932 and is attributable to $M^+ - CO$.

(11) Crystal data for **4**: $C_{45}H_{55}Cl_2OP_3W$, monoclinic, $P2_1/n$, a = 11.238 (3) Å, b = 18.527 (3) Å, c = 21.487 (2) Å, β = 103.27 (1)°, V = 4354 Å^3, Z = 4, D_{calcd} = 1.469 g cm^{-3}, μ(Mo Kα) = 29.83 cm^{-1}. A suitable single crystal of **4** was sealed in a Lindemann capillary under a nitrogen atmosphere and mounted on an Enraf-Nonius CAD 4 diffractometer. A total of 7568 unique reflections were collected (23 °C) in the range $2° < 2\theta < 50°$. Of these, 5068 reflections were considered observed ($I > 6.0\sigma(I)$) and were used to solve (Patterson) and refine (full-matrix, least squares) the structure of **4**. The final R and R_w values were 0.0324 and 0.0407, respectively.

(12) *Methods in Stereochemical Analysis. Vol. 8. Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers, Inc.: Deerfield Beach, FL, 1987.

(13) Yoshifuji, M.; Toyota, K.; Shibayama, K.; Inamoto, N. *Tetrahedron Lett.* **1984**, *25*, 1809.

Supplementary Material Available: Tables of bond lengths, angles, positional parameters, and thermal parameters for **4** (6 pages); table of observed and calculated structure factors for **4** (30 pages). Ordering information is given on any current masthead page.

Corner Attack on Cyclopropane by Thallium(III) Ions. A Highly Stereospecific Cleavage and Skeletal Rearrangement of 3α,5-Cyclo-5α-cholestan-6α-ol

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Two different mechanisms can be discerned for the electrophilic cleavage of cyclopropanes, namely, the "corner" or the "edge" attack by the electrophile,[1] resulting in the inversion or retention, respectively, at the center to which the electrophile becomes linked. Transition metals capable of back-donation (Pd, Pt, and Ir) favor the latter mechanism,[1,2] while mercury(II) ions and protons have recently been found to prefer the former reaction course.[3,4] Thallium(III) is another ion capable of the cleavage of cyclopropanes,[5] although only a few examples are known from the literature.[6] However, the stereochemistry and mechanism of these reactions have not been established and their synthetic potential is largely unexplored.

We report herein, for the first time, evidence for stereospecific corner attack at the cyclopropane ring by thallium(III), which is in line with the behavior of mercury(II) and contrasts with the oxidative edge addition of transition metals.

Treatment of model compound[7] **1** with $Tl(NO_3)_3 \cdot 3H_2O$ and a trace of $HClO_4$ in dioxane at room temperature for 5 h led to

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(1) (a) Coxon, J. M.; Battiste, M. A. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; J. Wiley and Sons: London, 1987; Chapter 6. (b) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

(2) (a) Dominelli, N.; Oehlschlager, A. C. *Can. J. Chem.* **1977**, *55*, 364. (b) Green, M.; Hughes, R. P. *J. Chem. Soc., Dalton Trans.* **1976**, 1880. (c) Wilhelm, D.; Bäckvall, J.-E.; Nordberg, R. E.; Norin, T. *Organometallics* **1985**, *4*, 1296 and references cited therein. (d) Bäckvall, J.-E.; Björkman, E. E.; Petersson, L.; Siegbahn, P.; Strich, A. *J. Am. Chem. Soc.* **1985**, *107*, 7408. (e) Nielsen, W. D.; Larsen, R. D.; Jennings, P. W. *J. Am. Chem. Soc.* **1988**, *110*, 8657. (f) Positively charged Pd species may prefer corner attack, so that two competing pathways can be encountered in certain instances. For a detailed discussion, see: (g) Blomberg, M. R. A.; Siegbahn, P. E. M.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1987**, *109*, 4450. (h) For the recent observation of "edge" halogenation, see: Lambert, J. B.; Chelius, E. C.; Schulz, W. J., Jr.; Carpenter, N. E. *J. Am. Chem. Soc.* **1990**, *112*, 3156.

(3) (a) Coxon, J. M.; Steel, P. J.; Whittington, B. I.; Battiste, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 2988; *J. Org. Chem.* **1989**, *54*, 1383. (b) Coxon, J. M.; Steel, P. J.; Whittington, B. I. *J. Org. Chem.* **1990**, *55*, 4136.

(4) (a) Collum, D. B.; Mohamadi, F.; Hallock, J. H. *J. Am. Chem. Soc.* **1983**, *105*, 6882. (b) Rood, I. D. C.; Klump, G. W. *Recl. Trav. Chim. Pays-Bas* **1984**, *103*, 303.

(5) (a) McKillop, A.; Taylor, E. C. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. VII, Chapter 47. Lead(IV) is also known to cleave the cyclopropane ring: (b) Criegee, R.; Rimmelin, A. *Chem. Ber.* **1957**, *90*, 417. (c) Ouelette, R. J.; Shaw, D. L. *J. Am. Chem. Soc.* **1964**, *86*, 1651.

(6) (a) Ouellette, R. J.; Shaw, D. L.; South, A., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 2744. (b) Campbell, H. M.; Gun, P. A.; McAlees, A. J.; McCrindle, R. *Can. J. Chem.* **1973**, *51*, 4167. (c) Salaun, J.; Garnier, B.; Conia, J. M. *Tetrahedron* **1974**, *30*, 1423. (d) Shirafuji, T.; Nozaki, H. *Tetrahedron* **1973**, *29*, 77. (e) Katsushima, T.; Yamaguchi, R.; Kawanishi, M.; Osawa, E. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3318. For examples in which cyclopropane was inert, see: (f) Sekizaki, H.; Ito, M.; Inoue, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2439.

(7) Wagner, A. F.; Wallis, E. S. *J. Am. Chem. Soc.* **1950**, *72*, 1047.

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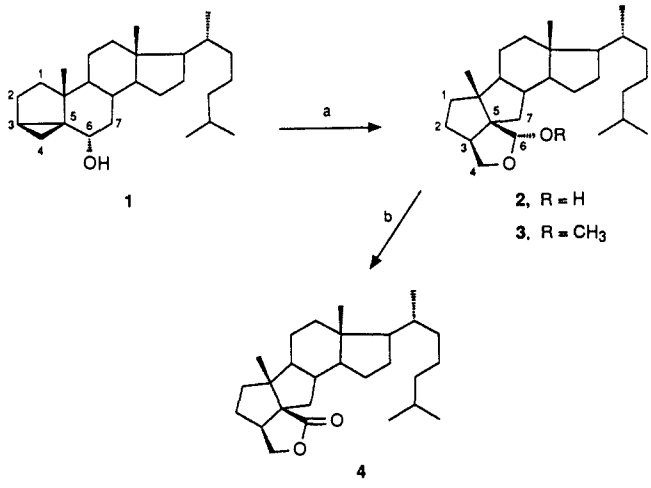
Scheme I[a]

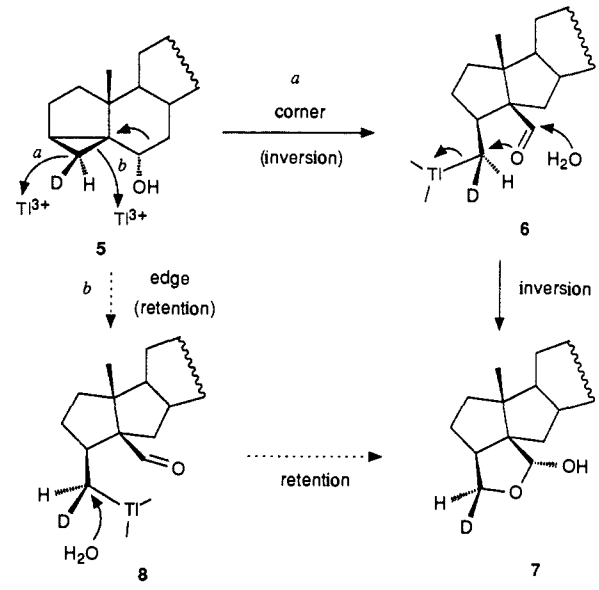


[a] (a) $Tl(NO_3)_3 \cdot 3H_2O$, dioxane, trace of $HClO_4$, room temperature, 5 h; (b) CrO_3, H_2SO_4, Me_2CO.

essentially a single product (later identified as **2**) in 63% isolated yield (Scheme I).[8] ^1H NMR, ^{13}C NMR, and IR spectra indicated the presence of a hemiacetal functionality of the type $CHCH_2OCHOH$.[9] Accordingly, an exchange reaction with methanol in the presence of a catalytic amount of HCl afforded methyl acetal **3**, while CrO_3 oxidation furnished γ-lactone **4**.[10] Connectivity in the "bottom" part of the hemiacetal species was established by H,H-COSY,[11] H,C-HETCOR,[12] and selective INEPT[13] NMR spectra, which revealed two fused five-membered rings with an annulated five-membered lactol. The upper part of the molecule remained unchanged. Hence, the structure of the hemiacetal in question was formulated as **2**.[14] Thus, the reaction of **1** with Tl(III) can be summarized as follows. The C_4–C_5 bond of the cyclopropane ring is cleaved[15] with concomitant migration of the antiperiplanar C_6–C_7 bond, and the reaction is completed by substitution of thallium by oxygen during the closure of the lactol ring.

Since the stereochemistry of the cyclopropane fission could not be established directly with **1**, a stereospecifically labeled compound **5** was synthesized[16] and subjected to the reaction with Tl(III) (Scheme II). Analysis of the ^1H NMR spectrum of the product **7** unequivocally established the configuration of deuterium as being 4β[18] and was indicative of a stereochemically homogeneous reaction as no other isomer could be detected. This result is in agreement with double inversion at C_4, i.e., with the initial "corner" cleavage of cyclopropane to give thalliated intermediate **6**, followed by S_N2 substitution by the neighboring carbonyl. The same product could be conjectured to arise from a double-retention pathway involving edge activation (**5** → **8**), and replacement of Tl with OH (from water) to give the corresponding alcohol, which would then spontaneously cyclize to lactol **7**. However, when the reaction of **1** with Tl(III) was run in dioxane containing water

Scheme II



enriched in ^{18}O by 25%, incorporation of the label was observed solely into the hydroxy group of the lactol **2**,[19] which further supports the double-inversion pathway shown in Scheme II. In a complementary experiment, the ^{18}O-labeled alcohol **1**[21] was treated with Tl(III). The product obtained (labeled **2**) had the label located solely in the ether oxygen,[22] which proves the carbonyl oxygen participation in the ring closure,[23] so that the double-retention mechanism can be ruled out.[24] These experiments thus provided conclusive evidence for the double-inversion pathway

(8) Compound **1** is inert to $HClO_4$ alone at room temperature, while a gradual conversion to cholesterol was observed at elevated temperature.

(9) IR: ν_{OH} = 3395, 3620 cm^{-1}. ^{13}C NMR (75.4 MHz): 101.16 ppm.

(10) IR: ν_{CO} = 1755 cm^{-1}. ^{13}C NMR: δ 182.13 ppm.

(11) Bax, A.; Freeman, R.; Morris, G. A. *J. Magn. Reson.* **1981**, *42*, 164.

(12) Reynolds, W. F.; McLean, S.; Perpick-Dumont, M.; Enriquez, R. G. *Magn. Reson. Chem.* **1988**, *26*, 1068.

(13) Bax, A. *J. Magn. Reson.* **1984**, *57*, 314.

(14) The full assignment of carbon signals in the ^{13}C NMR spectrum of **3** has been achieved.

(15) Note that the cleavage occurs regioselectively between the most and the least substituted carbon. In view of a recent observation of similar regioselectivity for Hg(II)[3], this seems to be a general reactivity pattern of cyclopropanes toward nontransition metals.

(16) Deuterated **5** was prepared in four steps from the known[17] 4β-deuteriocholesterol, analogously to its unlabeled congener **1** (see ref 7).

(17) Nambara, T.; Ikegawa, S.; Ishizuka, T.; Goto, J. *J. Pharm. Bull.* **1974**, *22*, 2656.

(18) In the ^1H NMR spectrum of **7**, 4α-H appears at 4.15 (d, J = 9.2 Hz) and shows an NOE (17%) upon irradiation of 3α-H.

(19) The mass spectrum of the product revealed 13.6 ± 0.8% incorporation of ^{18}O, which could be quantitatively washed out by H^+/H_2O so that the label cannot be located in the ether oxygen. Moreover, two signals were observed for the acetal carbon in the ^{13}C NMR spectrum at 101.18 and 101.21 ppm due to the ^{18}O isotope effect, whereas only one signal was detected for C_4 (at 72.01 ppm).[20]

(20) For determination of the ^{18}O distribution in various groups by ^{13}C NMR, see: (a) Vederas, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 374. (b) Kočovský, P.; Tureček, F. *Tetrahedron* **1983**, *39*, 3621. (c) Hansen, P. E. *Annual Reports on NMR Spectroscopy*; Academic: London, 1983; Vol. 15, p 106.

(21) The ^{18}O-labeled 6α-alcohol was prepared from 3,5-cyclo-5α-cholestan-6-one. Acid-catalyzed exchange with water enriched in ^{18}O by 25% afforded the labeled ketone (MS, 18 ± 0.7% of ^{18}O; IR, $\nu_{C=O}$ = 1684, $\nu_{C=O}$ = 1654 cm^{-1}), reduction of which with $LiAlH_4$ gave the [6-^{18}O]-3,5-cyclo-5α-cholestan-6α-ol.

(22) The mass spectrum of the labeled lactol showed 18 ± 0.9% of ^{18}O, and the label could not be washed out with H^+/H_2O. The lactone prepared by oxidation of the lactol had the same content of the label. The ^{13}C NMR spectrum of the lactone exhibited two twin signals for the COC=O unit (δ 69.25, 69.28, 182.11, and 182.13 ppm) consistent with the expected isotope effect of ^{18}O.[20]

(23) Intramolecular nucleophilic participation by the ketone or aldehyde carbonyl is quite common. For further examples, see: (a) Capon, B.; McManus, S. P. *Neighboring Group Participation*; Plenum: New York, 1976; Vol. 1. (b) Kočovský, P.; Tureček, F.; Hájíček, J. *Synthesis of Natural Products: Problems of Stereoselectivity*; CRC: Boca Raton, FL, 1986. (c) Baddeley, G.; Baylis, E. K.; Heaton, B. G.; Rasburn, J. W. *Proc. Chem. Soc. London* **1961**, 451. (d) Reist, E. J.; Tan, M. *Carbohydr. Res.* **1971**, *18*, 446. (e) Brimacombe, J. S.; Hunedy, F.; Tucker, L. C. N. *J. Chem. Soc. C* **1968**, 1381. (f) Shapiro, E. L.; Weber, L.; Polovsky, S.; Morton, J.; McPhail, A. T.; Onan, K. D.; Barton, D. H. R. *J. Org. Chem.* **1976**, *41*, 3940. (g) Wolff, S.; Agosta, W. C. *Tetrahedron Lett.* **1985**, *26*, 703. (h) Mehta, G.; Prakasa Rao, H. S. *J. Chem. Soc., Chem. Commun.* **1986**, 472. For representative examples of other carbonyl-type participation, see: (i) Kočovský, P.; Stieborová, I. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1969.

(24) Nucleophilic S_N2-type displacement of the thallium species appears to be a common reaction and is well documented.[25] Another mechanism, which would involve the carbonyl oxygen coordination to thallium (in **8**) followed by reductive elimination (as suggested by a referee), is extremely unlikely for a nontransition metal such as thallium. One might rather expect the formation of a C–C bond in a Grignard or Tebbe-like reaction, which, however, does not occur either.

(25) (a) Michael, J. P.; Ting, P. C.; Bartlett, P. A. *J. Org. Chem.* **1985**, *50*, 2416. (b) Michael, J. P.; Nkwelo, M. M. *Tetrahedron* **1990**, *46*, 2549. (c) Ferraz, H. M. C.; Brocksom, T. J.; Pinto, A. C.; Abla, M. A.; Zocher, D. H. T. *Tetrahedron Lett.* **1986**, *27*, 811. (d) Kočovský, P.; Langer, V.; Gogoll, A. *J. Chem. Soc., Chem. Commun.* **1990**, 1026.

involving "*corner*" *activation of the cyclopropane ring by* Tl(III).

The attack of the thallic ion at the "corner" of the cyclopropane parallels the reactivity of the mercuric ion and the proton, allowing similar orbital arguments[3] to be used. Neither Hg^{2+} nor Tl^{3+} is a good back-donor so that the back-donation of their d_π electrons to the LUMO Walsh orbital is negligible; therefore the "edge" activation is apparently disfavored. On the other hand, the observed corner attack by Tl^{3+} (and Hg^{2+}) reflects the favorable interaction of the degenerate HOMOs of the cyclopropane with vacant d orbitals on the metal. Our experiments thus provide further support for the mechanistic picture and orbital considerations recently published by Coxon et al.[3] We are confident that our results furnish an additional example required for the generalization of the original rationalization[3] which was derived from the behavior of only one nontransition metal. Moreover, the rearrangement of the cyclopropyl alcohol **1** represents an attractive synthetic avenue for the stereoselective construction of the oxa-triquinane skeleton or of spirocyclic lactones. Although the experiments were confined to the steroidal skeleton, we believe that our finding is of a general nature and might be used as the key step for the construction of complex natural products.

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Supplementary Material Available: Melting points and IR, ^1H NMR, ^{13}C NMR, MS, and analytical data for **2-4** and **7** (2 pages). Ordering information is given on any current masthead page.

Carbonyl-Ene Reaction with Vinylsilanes: Silicon as a Controlling Element for Regio- and Stereochemistry

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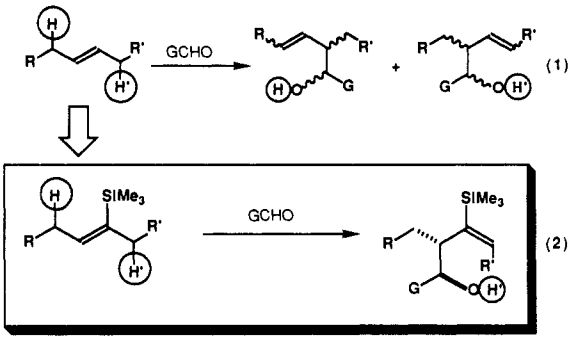
Received February 9, 1990

Control of the sites of C-H bond activation and C-C bond formation is of current interest for synthetic exploitation in carbon skeletal construction. In principle, the ene reaction involving carbonyl enophiles (Scheme I) is the simplest way for C-C bond formation, which converts readily available alkenes, with substitution for allylic C-H bond and allylic transposition of the C=C bond, into more functionally complex derivatives.[1] However, the synthetic utility of the carbonyl-ene reaction has been overshadowed by the lack of regioselectivity when applied to unsymmetrical alkenes (eq 1).

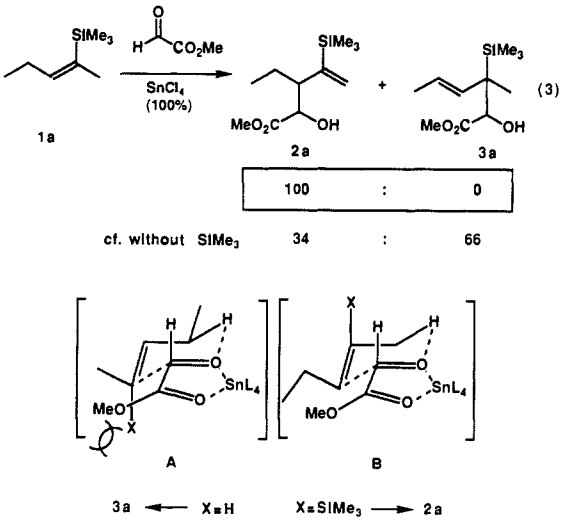
Herein we report the first example of the Lewis acid promoted carbonyl-ene reaction with vinylsilane as an ene,[2] which provides a solution to this regiochemical problem and constitutes a highly stereocontrolled version of a carbonyl-ene reaction (eq 2). The key feature in the regio- and stereochemical control of the concerted process[3] lies in the steric bulkiness of the trialkylsilyl group.[4]

Scheme I



The great advantages of the present version of the carbonyl-ene reaction are (1) *the highly regiocontrolled introduction of a potential functionality based on vinylsilane*[4] and (2) *the remarkable enhancement of diastereoselectivity and the dramatic changeover in olefinic stereoselectivity.*

First, the use of vinylsilane (**1**)[5] as an ene is found to alter the regiochemical course in the glyoxylate-ene reaction to give the vinylsilane product **2** as a *single* regioisomer (eq 3).[6] The highly



regiocontrolled ene reaction with vinylsilane is in sharp contrast to the ene reaction with 1,2-disubstituted alkene without a silyl group, which gives a mixture of regioisomers under the same reaction conditions.[7] The observed regiocontrol can be explained on the basis of the six-membered transition-state model[8] by an enhanced steric interaction of $SiMe_3$ and CO_2Me relative to that of H and CO_2Me in A. Thus, the vinylsilane **2a** would be formed regioselectively via the transition state B.

(1) Reviews on intermolecular ene reactions: (a) Mikami, K.; Terada, M.; Shimizu, M.; Nakai, T. *J. Synth. Org. Chem. Jpn.* **1990**, *48*, 292. (b) Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426. (c) Hoffman, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556. (d) Whitesell, J. K. *Acc. Chem. Res.* **1985**, *18*, 280.

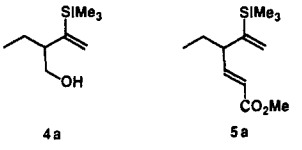
(2) Review on ene and retro-ene reactions in group 14 organometallic chemistry: Dubac, J.; Laporterie, A. *Chem. Rev.* **1987**, *87*, 319.

(3) The mechanism of Lewis acid promoted ene reactions has been the subject of controversial discussions (a concerted pericyclic vs stepwise cationic mechanism): Snider, B. B.; Ron, E. *J. Am. Chem. Soc.* **1985**, *107*, 8160, and references therein. However, a cationic reaction with vinylsilane should provide the other substitution product via a favorable β-silyl cation,[4] not the ene-type product arising from an unfavorable α-silyl cation. Thus, the present reaction with vinylsilane might provide a novel probe for the mechanism of the Lewis acid promoted ene reactions.

(4) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981; Chapter 2. Fleming, I. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon: Oxford, 1979; Vol. 3, Part 13. Magnus, P. D.; Sarkar, T.; Djuric, S. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 7, Chapter 48.

(5) Vinylsilanes are prepared following the literature procedure: Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988, Chapter 3, and references therein.

(6) A high level of regiocontrol is also found in the ene reaction of formaldehyde or propiolate to give the single ene product **4** or **5**, respectively.



4a 5a

(7) A methylene hydrogen has been reported to be twice as reactive as a methyl or methine hydrogen after correction for statistical factors.[1]

(8) Mikami, K.; Loh, T.-P.; Nakai, T. *Tetrahedron Lett.* **1988**, *29*, 6305.

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