

mass spectrum, m/z (relative intensity) 627 (8), 585 (26), 543 (22), 42 (100); HRMS, obsd m/z 627.1711, $C_{34}H_{29}NO_{11}$ requires m/z 627.1739.

Diacetate 7: UV (MeOH) 337 (sh), 312, 278, 268 (sh), 229 nm; 1H NMR ($CDCl_3$) δ 2.31 (s, 3 H), 2.35 (s, 3 H), 3.16 (m, 2 H), 3.37 (s, 3 H), 3.43 (s, 3 H), 3.81 (s, 3 H), 3.87 (s, 3 H), 3.90 (s, 3 H), 4.76 (m, 1 H), 4.82 (m, 1 H), 6.54 (s, 1 H), 6.69 (s, 1 H), 7.10 (s, 1 H), 7.10 (d, 1 H, $J = 1.7$ Hz), 7.13 (dd, 1 H, $J = 8, 1.7$ Hz), 7.22 (d, 1 H, $J = 8$ Hz); mass spectrum, m/z (relative intensity) 629 (28), 587 (100), 545 (76), 530 (36); HRMS, obsd m/z 629.1932, $C_{34}H_{31}NO_{11}$ requires m/z 629.1896.

Triacetate 8: UV (MeOH) 384, 364, 345, 335 (sh), 320 (sh), 308 (sh), 300 (sh), 282, 232 nm; 1H NMR ($CDCl_3$) δ 2.33 (s, 3 H), 2.35 (s, 3 H), 2.37 (s, 3 H), 3.45 (s, 6 H), 3.84 (s, 3 H), 6.81 (s, 1 H), 7.08 (d, 1 H, $J = 7.4$ Hz), 7.17 (s, 1 H), 7.20 (d, 1 H, $J = 1.8$ Hz), 7.22 (s, 1 H), 7.23 (dd, 1 H, $J = 8, 1.8$ Hz), 7.30 (d, 1 H, $J = 8$ Hz), 7.41 (s, 1 H), 9.25 (d, 1 H, $J = 7.4$ Hz); mass spectrum, m/z (relative intensity) 625 (29), 583 (40), 541 (100), 499 (91); HRMS, obsd m/z 625.1638,

$C_{34}H_{27}NO_{11}$ requires m/z 625.1584.

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Registry No. *anti*-1, 97614-62-5; *syn*-1, 97672-36-1; 2, 97614-63-6; 3, 97614-64-7; 4, 97614-65-8; *anti*-5, 97614-66-9; *syn*-5, 97672-37-2; 6, 97614-67-0; 7, 97614-68-1; 8, 97633-82-4.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond distances, and bond angles for lamellarin A (5 pages). Ordering information is given on any current masthead page.

General Method for Generation of 3-Siloxyallylmetallic Species and Their Synthetic Application

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Contribution from Department of Chemistry, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan. Received April 1, 1985

Abstract: On treatment with vinylmagnesium bromide, most of the α -branched acyltrimethylsilanes initially form the corresponding 1-(trimethylsilyl)allylic alkoxides, which undergo a facile rearrangement of the silyl group from carbon to oxygen to generate 3-(trimethylsiloxy)allylmagnesium bromides, namely, homoenolate equivalents, almost quantitatively. On the other hand, use of alcohols prepared from acyl(*tert*-butyl)dimethylsilanes has made it feasible to generate lithium homoenolate equivalents bearing straight side chains. Thus, treatment of 1-(*tert*-butyldimethylsilyl)allylic alcohols with an equimolar amount of butyllithium in THF has allowed generation of the corresponding lithium homoenolates in over 80% yield irrespective of difference of electronegativities between carbon and oxygen. Under the influence of copper(I) trimethylsilylacetylide, these reagents add to enones to give the corresponding 1,6-diketone derivatives bearing enol ether moieties, which can further serve for introduction of other electrophiles or unsaturation. Oxiranes also react with these copper homoenolates to yield the corresponding 5-hydroxy ketone derivatives.

Although enolate anions have been extensively studied in synthetic organic chemistry, the characteristics and behavior of their homologous nucleophiles, namely, homoenolate anions,¹ have not been so fully elucidated up to now. Recently, their synthetic utility has been well recognized, and several studies on this subject have been described by us² and others.^{3,4} These nucleophiles reported hitherto can be classified into two types: metal homoenolates themselves and their synthetic equivalents. A few reports have appeared on the former and several synthetic reactions using such species as nucleophiles have been described, but some limitations exist from a synthetic viewpoint on such aspects as structural limitations as well as rather poor nucleophilicities attributable to the nature of counter metal cations.^{2,3}

Recent progress achieved by using organosilicon compounds has offered several new aspects to synthetic organic chemistry.⁵ One of them is an introduction of enol silyl ethers⁶ as enolate equivalents, which has brought about a great contribution to regiocontrol of enolate chemistry. Another interesting feature on synthetic background is expected from a possibility of generating several types of carbanionic species from the metal alkoxides through the so-called Brook-West rearrangement.⁷ Based on these features we studied the generation of metal homoenolate equivalents⁸ bearing enol silyl ether moieties as the masked carbonyl functionality from 1-(trimethylsilyl)allylic alcohols which can easily be prepared from acyltrimethylsilanes^{9,10} with vinylmagnesium halide. In the previous paper, we reported alkylation

(1) Review: Werstiuk, N. H. *Tetrahedron* **1983**, 39, 205.

(2) Titanium homoenolates of esters: Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1977**, 99, 7360. Zinc homoenolates of esters: Nakamura, E.; Kuwajima, I. *Ibid.* **1984**, 106, 3368. Homo enolates of main metal group: Nakamura, E.; Shimada, J.; Kuwajima, I. *Organometallics* **1985**, 4, 641.

(3) (a) Caine, D.; Frobest, A. S. *Tetrahedron Lett.* **1978**, 883. (b) Goswami, R.; Corcoran, D. E. *Ibid.* **1982**, 23, 1463. (c) Goswami, R.; Corcoran, D. E. *J. Am. Chem. Soc.* **1983**, 105, 7182. (d) Ryu, I.; Ando, M.; Ogawa, A.; Murai, S.; Sonoda, A. *Ibid.* **1983**, 105, 7192.

(4) Homo enolate equivalents: (a) Evans, D. A.; Andrews, G. C.; Buckwalter, B. *J. Am. Chem. Soc.* **1974**, 96, 5560. (b) Still, W. C.; Macdonald, T. L. *Ibid.* **1974**, 96, 5561. (c) Lesur, B.; Toye, J.; Chantrenne, M.; Ghosez, L. *Tetrahedron Lett.* **1979**, 2835. (d) De Lombaert, S.; Lesur, B.; Ghosez, L. *Ibid.* **1982**, 23, 4251.

(5) (a) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, 1981. (b) Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: Berlin, 1983.

(6) Brownbridge, P. *Synthesis* **1983**, 1, 85. Reference 5a, pp 198-287. Reference 5b, pp 206-272.

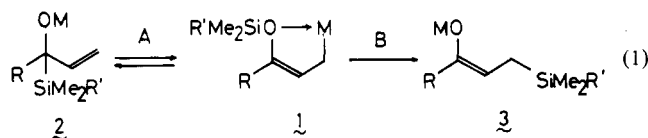
(7) Brook, A. G. *Acc. Chem. Res.* **1974**, 7, 77.

(8) Kuwajima, I.; Kato, M. *J. Chem. Soc., Chem. Commun.* **1979**, 708. Kato, M.; Mori, A.; Oshino, H.; Enda, J.; Kobayashi, K.; Kuwajima, I. *J. Am. Chem. Soc.* **1984**, 106, 1773.

(9) Kuwajima, I.; Abe, T.; Minami, N. *Chem. Lett.* **1976**, 993. Kuwajima, I.; Arai, M.; Sato, T. *J. Am. Chem. Soc.* **1977**, 99, 4181. Kuwajima, I.; Kato, M.; Sato, T. *J. Chem. Soc., Chem. Commun.* **1978**, 478. Kuwajima, I.; Mori, A.; Kato, M. *Bull. Chem. Soc. Jpn.* **1980**, 53, 2368.

(10) Cohen, T.; Matz, J. R. *J. Am. Chem. Soc.* **1980**, 102, 6900.

reactions of such homoenolate equivalents,⁸ which led to a stereo- and regio-defined synthesis of enol silyl ethers. For their general synthetic use, however, two problems still remain to be solved. First, the great difference of electronegativities between oxygen and carbon has greatly disfavored the formation of the desired homoenolates **1**⁸ in synthetically acceptable amounts which has made it impossible to use them as precursors for other organometallics such as organocopper reagents. A facile and irreversible



rearrangement¹¹ (B) of **1** to the lithium enolates of β -trimethylsilyl ketones **3** ($R' = \text{CH}_3$) is another drawback to prevent synthetic use of **1**. In the present paper we describe a useful methodology for predominant or sometimes stoichiometric generation of homoenolate **1**,¹² which cleanly undergoes transmetalation to form an organocopper species to use for conjugate addition to enones, and ring opening of oxiranes.

Results and Discussion

It has generally been believed that the Brook-type rearrangement (A) is effected under the influence of a catalytic amount of a base under equilibrium conditions in which the resulting carbanionic species undergo a rapid protonation to shift the equilibrium to the carbanionic side,^{7,8,13} but generation of such a carbanionic species⁷ in synthetically acceptable yield is almost impossible because of the much greater electronegativity of the oxide anion. However, we have disclosed the fact that several types of 3-siloxyallyl anionic species can be generated quite efficiently by structural modifications of the starting alcohols **2**. Organosilyl groups are expected to behave as sterically hindered groups, and a further introduction of another sterically demanding group closely situated to the carbon attached to the silyl and oxide anion may cause a severe steric repulsion between these groups to facilitate the rearrangement of silyl group from carbon to less sterically hindered oxide anions. During this investigation which was based on such assumptions, it was found that treatment of 2-ethylbutyryltrimethylsilane with vinylmagnesium bromide in tetrahydrofuran (THF) and subsequent quenching of the reaction mixture afforded the corresponding enol silyl ether exclusively. As the solvent, THF seems to be essential to induce such rearrangement, and ether did not effect the conversion to give back the corresponding alcohol **2** exclusively. On the other hand, use of 2-methylbutyryltrimethylsilane or cyclohexanecarbonyltrimethylsilane usually afforded a mixture of the corresponding 1-(trimethylsilyl)allylic alcohols **2** and enol silyl ethers. The ratio of the silyl ether to the alcohol **2** observed here can be interpreted to reflect an equilibrium composition of the homoenolate **1** ($M = \text{MgBr}$, $R' = \text{CH}_3$) and alkoxide. Thus, these results clearly indicate that magnesium alkoxides of some allylic alcohols **2** initially formed are rapidly converted to the desired homoenolates **1** sometimes in stoichiometric amount regardless of an expected disadvantage due to the difference of electronegativity.

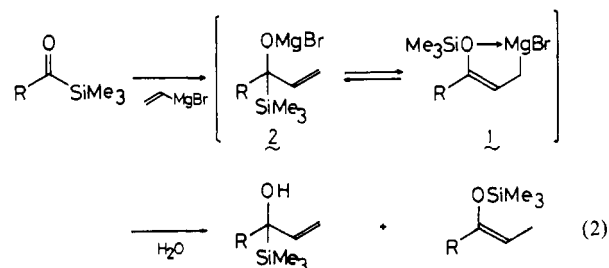
In these cases, use of a magnesium cation in place of lithium appears to be very crucial to retard the irreversible rearrangement (B) of the resulting **1** to the β -silyl ketones **3**. When lithium alkoxides are used, formation of enolates of **3** takes place quite rapidly under similar reaction conditions to give, on quenching, a complex mixture of the enol silyl ether, β -silyl ketone **3**, and sometimes the parent alcohol **1**. The difference observed between lithium and magnesium homoenolates may be due to the less ionic character of a carbon-magnesium bond, which makes it infeasible

Table I. Compositions of 3-(Trimethylsiloxy)allylmagnesium Bromides **1** ($M = \text{MgBr}$, $R' = \text{CH}_3$) and Magnesium Alkoxides of **2** ($R' = \text{CH}_3$)^a

R	yield (%)	
	alcohol 2	enol silyl ether
C_5H_{11}	100	0
$(\text{C}_2\text{H}_5)_2\text{CH}$	0	100
$\text{C}_3\text{H}_7\text{CH}(\text{CH}_3)$	63	37
$\text{Me}_3\text{SiCH}_2\text{CH}(\text{CH}_3)$	35	65
cyclohexyl	50	50
$\text{C}_6\text{H}_5\text{CH}(\text{C}_2\text{H}_5)$	0	100
$\text{C}_6\text{H}_5\text{CH}(i\text{-Pr})$	0	100

^a The composition was determined by GLC analysis of the solution obtained by treating the corresponding acyltrimethylsilanes with vinylmagnesium bromide in THF at room temperature for 1 h followed by quenching the reaction mixture.

to attack the silicon atom to form **3**. As shown in Table I, use of several acyltrimethylsilanes has allowed a stoichiometric generation of the magnesium homoenolate **1** ($M = \text{MgBr}$, $R' = \text{CH}_3$) just by treatment with vinylmagnesium bromide in THF at an ambient temperature. At least two alkyl groups larger than ethyl appear to be required on their 2-positions for complete formation of **1**. A phenyl group can be replaced with an ethyl group; use of 2-phenylbutyryltrimethylsilane also leads to the quantitative generation of the corresponding **1**. Irrespective of such structural limitations, they can be employed as useful nucleophiles for several synthetic purposes as shown later.



This great influence of steric factors to determine the equilibrium composition of **1** and the alkoxide has also suggested the possibility that introduction of a certain bulky group on the silicon atom itself may also favor the formation of the desired homoenolate which would further broaden the scope of the present procedure because a structural limitation might be removed from major carbon frameworks. 1-Decen-3-ols possessing various silyl groups at their 3-positions were prepared and tendencies to rearrange were examined using their magnesium and lithium alkoxides. Requisite acylsilanes bearing several types of alkyldimethylsilyl or triethylsilyl groups were prepared in good yield by a procedure similar to that for prototypal derivatives.^{9,10} While triethyl-, isopropylidimethyl-, and *sec*-butyldimethylsilyl groups are not enough to effect the generation of magnesium homoenolates, introduction of a *tert*-butyldimethylsilyl group has allowed generation of the corresponding **1** ($M = \text{MgBr}$, $R' = t\text{-Bu}$) in 61% yield together with the parent alkoxides. We were pleased to find that lithium alkoxides greatly improved the situation and **1** has been formed as a major component. Especially on using *tert*-butyldimethylsilyl derivatives, the desired homoenolates **1** ($M = \text{Li}$, $R' = t\text{-Bu}$) can be generated over 80% yield on standing in THF at low temperature. Although a small amount of the β -silyl ketone is also formed, it can be minimized by controlling the reaction temperature. In contrast to a facile conversion of trimethylsilyl derivatives to **3**, such an irreversible rearrangement as (B) appears to occur very slowly and most of **1** survives even after standing at 0 °C for 30 min.¹⁴ The much less mobile character of the *tert*-butyldimethylsilyl group may be responsible for such a phenomenon. The chain length of the parent alcohol

(11) Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063. Still, W. C.; Mitra, A. *Tetrahedron Lett.* **1978**, 2659.

(12) Enda, J.; Matsutani, T.; Kuwajima, I. *Tetrahedron Lett.* **1984**, *25*, 5307.

(13) Kuwajima, I.; Kato, M. *Tetrahedron Lett.* **1980**, *21*, 623. Kato, M.; Kuwajima, I. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 827. See also: Reich, H. J.; Olson, R. E.; Clark, M. C. *J. Am. Chem. Soc.* **1980**, *102*, 1423.

(14) An irreversible rearrangement of **1** ($M = \text{Li}$, $R = \text{C}_7\text{H}_{15}$, $R' = t\text{-Bu}$) takes place slowly at room temperature and gave the corresponding **3** in 88% yield after standing for 10 h.

Table II. Compositions of Metal Alkoxides of 3-(Alkyldimethylsilyl)-1-decen-3-ol and Its Metal Homoenoates

1		temp, °C	yield (%)	
R'	M		alcohol	enol silyl ether
<i>n</i> -C ₄ H ₉	MgBr	r.t.	100	0 ^a
<i>i</i> -C ₄ H ₉	MgBr	r.t.	100	0 ^a
<i>sec</i> -C ₄ H ₉	MgBr	r.t.	100	0 ^a
<i>sec</i> -C ₄ H ₉	Li	-70	100	0 ^b
<i>sec</i> -C ₄ H ₉	Li	0	27	73 ^b
<i>sec</i> -C ₄ H ₉	Li	0	28	72 ^c
<i>t</i> -C ₄ H ₉	MgBr	r.t.	39	61 ^a
<i>t</i> -C ₄ H ₉	Li	-70	7	87 ^{b,d}
<i>t</i> -C ₄ H ₉	Li	0	6	82 ^{b,e}
<i>sec</i> -C ₅ H ₁₁	MgBr	r.t.	100	0 ^a
C ₆ H ₅	MgBr	r.t.	100	0 ^a

^a The composition was determined by a similar procedure described on the footnote of Table I. ^b The composition was determined by GLC analysis of the solution obtained by standing the lithium alkoxide in THF for 30 min followed by quenching the resulting solution. ^c The composition was determined on the solution obtained by standing at 0 °C for 30 min and then at -70 °C for 1 h. ^d 1-(*tert*-Butyldimethylsilyl)-3-decanone was also formed in 6%. ^e The ketone above was also formed in 12%.

Table III. Compositions of Lithium Alkoxides of 1-(*tert*-Butyldimethylsilyl)allylic Alcohols and Their Lithium Homoenoates^a

R	yield (%)	
	alcohol	enol silyl ether
CH ₃	60	40
C ₂ H ₅	15	80 ^b
C ₇ H ₁₅	6	82 ^c

^a The composition was determined by a similar procedure on the solution after standing for 30 min at 0 °C. ^b The corresponding β -silyl ketone **3** was formed in 5% yield. ^c The β -silyl ketone **3** was formed in 12% yield.

also has an influence on generation of the corresponding **1**. For example, 2-(*tert*-butyldimethylsilyl)-3-buten-2-ol gave a mixture of **1** and the alkoxide, whereas its higher homologues such as 3-silyl-1-penten-3-ol afforded the silyl enol ether predominantly, as confirmed by quenching the resulting solution. Thus, with a few exceptional cases (R = H or CH₃ of **1**), this method can be generally employed for generation of this type of lithium homoenoates **1** in over 80% yields.

Based on the success of stoichiometric or predominant generation of **1**, we next examined transformation of these magnesium homoenoates to copper(I) reagents. However, we were surprised to find it very difficult to control conjugate addition of these homoenoate species even in the presence of several copper(I) salts.¹⁵ Copper(I) halides, cyanide, and their tributylphosphine complexes all failed to effect this addition reaction. Copper(I) butylacetylide and cuprous bromide-dimethyl sulfide complex are only slightly effective; the former effects the conjugate addition of **1** (M = Li, R = C₇H₁₅, R' = CH₃) to cyclohexenone in 19% yield and the latter in 20% yield. House and Wilkins¹⁶ also found it is almost impossible to effect selective conjugate addition of allylmagnesium species in the presence of various Cu(I) salts. A great difference between usual allylmagnesium species and **1** is that 1,2-addition occurs predominantly with the former, whereas the nucleophilicity of the latter is very poor in the presence of several Cu(I) salts, giving back the protonated enol silyl ethers even after prolonged reaction period or at higher reaction temperature. After several attempts with various Cu(I) salts, copper(I) trimethylsilylacetylide proved to be very efficient in effecting the conjugate addition of magnesium homoenoate species. On treatment with several enones, the corresponding 1,6-diketone derivatives are obtained in good yield. The products can be isolated

Table IV. Conjugate Addition of Magnesium Homoenoates **1** to Enones in the Presence of Copper Trimethylsilylacetylide^a

enones	R	product	yield (%)
cyclohexenone	(C ₂ H ₅) ₂ CH	4a	86
	C ₆ H ₅ CH(C ₂ H ₅)	4b	84 (90 ^b)
	C ₆ H ₅ CH(<i>i</i> -C ₃ H ₇)	4c	88 ^c
3-methylcyclohexenone	C ₆ H ₅ CH(C ₂ H ₅)	4d	74
	C ₆ H ₅ CH(<i>i</i> -C ₃ H ₇)	4e	78 ^c
3-hepten-2-one	C ₆ H ₅ CH(C ₂ H ₅)	4f	64, 96 ^d
	C ₆ H ₅ CH(<i>i</i> -C ₃ H ₇)	4g	65 ^c
heptenal	C ₆ H ₅ CH(C ₂ H ₅)	4h	49 ^d
ethyl acrylate	C ₆ H ₅ CH(C ₂ H ₅)	4i	58 ^e
ethyl 2-heptenoate	C ₆ H ₅ CH(C ₂ H ₅)	4j	49 ^f

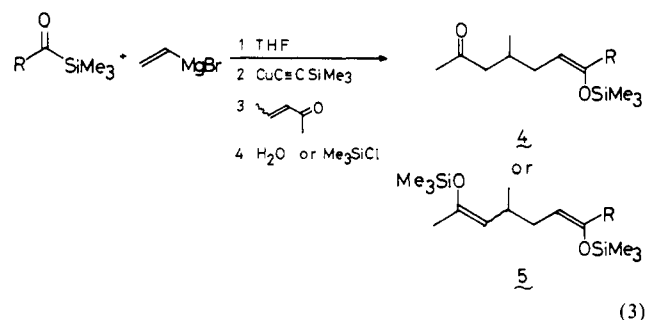
^a Reactions were performed according to the procedure described in the Experimental Section, unless otherwise noted. ^b The number in parentheses represents the yield of bis-silyl enol ether **5**. ^c The product was isolated as the corresponding 1,6-diketone. ^d The reaction was performed with 1.5 equiv of the homoenoate and copper trimethylsilylacetylide. ^e The reaction was carried out with 2 equiv of the homoenoate and copper trimethylsilylacetylide in ether for 6 h at -20 °C. ^f The reaction was carried out for 9 h at 0 °C.

Table V. Conjugate Addition of Lithium Homoenoates **1** to Enones in the Presence of Copper Trimethylsilylacetylide^a

enone	R	product	yield (%)
cyclohexenone	CH ₃	7a	43, 80 ^c
	C ₂ H ₅	7b	92 (88 ^d)
	C ₇ H ₁₅	7c	82 (76 ^d)
3-methylcyclohexenone	C ₂ H ₅	7d	77
	C ₇ H ₁₅	7e	88
methyl vinyl ketone	C ₇ H ₁₅	6f	(62 ^d)
3-hepten-2-one	C ₂ H ₅	7g	51
	C ₇ H ₁₅	7h	61 (13 ^d)

^a Reactions were performed according to procedure A or B described in Experimental Section, unless otherwise noted. ^b The reaction was performed in the presence of HMPA. ^c The reaction was carried out with 2 equiv of the homoenoate and copper trimethylsilylacetylide in the presence of HMPA. ^d Numbers in parentheses represent the yields of monosilyl enol ethers **6**.

as their monosilyl enol ethers **4** as well as bis-silyl ethers **5** depending on the workup procedure. An α,β -unsaturated ester can also be employed as the conjugate addition acceptor with less efficacy.

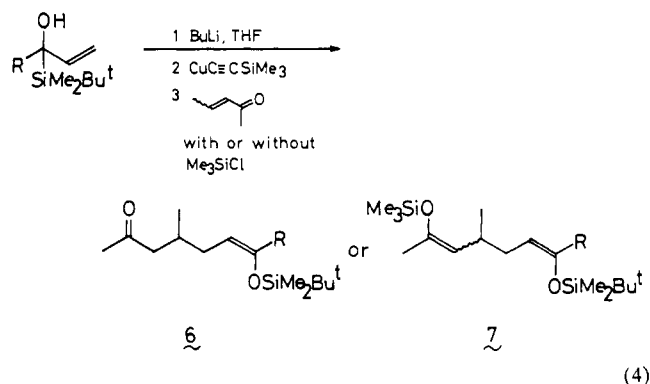


In the presence of the copper(I) trimethylsilylacetylide, lithium homoenoates **1** (M = Li, R' = *t*-Bu) also undergo conjugate addition cleanly to yield **6**. The 3-(*tert*-butyldimethylsiloxy)-2-butenyl moiety can also be introduced in good yield by using 2 equiv of the parent alcohol **2** (R = CH₃, R' = *t*-Bu). It should be noted here that chlorotrimethylsilane generally facilitates the conjugate addition,¹⁷ and its remarkable effect has been observed on the homoenoates derived from 3-(*tert*-butyldimethylsiloxy)-allyllithiums to afford the corresponding products as their bis-silylated enol ethers **7**. Different from magnesium species, lithium homoenoates did not react with an unsaturated ester even in the presence of the copper(I) acetylide and chlorotrimethylsilane. The results are summarized in Table V.

(15) Posner, G. H. *Org. React.* **1972**, *19*, 1. Posner, G. H. "An Introduction to Synthesis Using Organocopper Reagents"; Wiley: New York, 1980.

(16) House, H. O.; Wilkins, J. M. *J. Org. Chem.* **1978**, *43*, 2443.

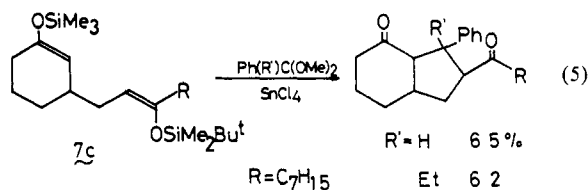
(17) Unpublished results by Y. Horiguchi and S. Matsuzawa in our laboratory.



Several synthetic transformations have also been performed on the resulting addition products as follows. The mono-silyl ethers can be transformed to the enedione such as **8** selectively on treatment with Pd(II) as reported by Ito et al.¹⁸ Application to an appropriately substituted cyclopentenone may provide a useful alternative for prostaglandin synthesis¹⁹ because the *E* olefinic linkage can be selectively introduced by such a procedure. Similar treatment of bis-silyl enol ethers gave the corresponding diene dione **9**. *tert*-Butyldimethylsilyl enol ethers also undergo such transformation with rates similar to those of trimethylsilyl enol ethers.²⁰

A certain electronic factor prevents the generation of γ -substituted homoenolate species. For example, neither 5-phenyl-4-(trimethylsilyl)-2-hepten-4-ol nor 4-(*tert*-butyldimethylsilyl)-2-undecen-4-ol underwent this type of rearrangement under the present reaction conditions and the alcohols were recovered. However, selective introduction of several alkyl groups on such position can be performed via conjugate addition of organocopper species by using the resulting enedione substrates such as **8**, which compensates for the failure of generation of alkyl-substituted anionic species.

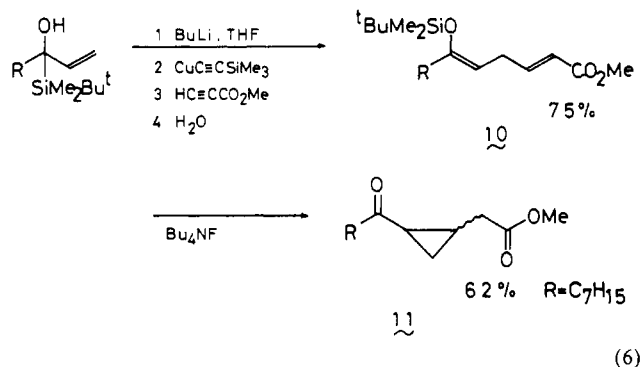
Further, bis-silyl enol ethers **7** behave in a unique manner on treatment with aromatic acetals.²¹ Under the influence of tin(IV) chloride, they connect two enol ether moieties through themselves to afford the cyclopentane annulation products. The reaction



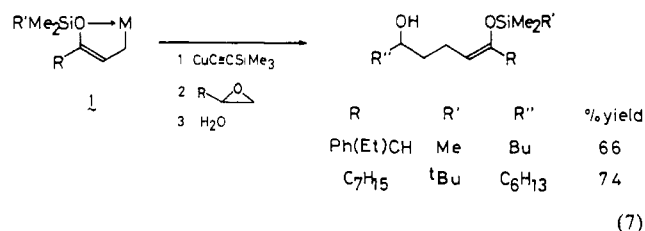
is considered to proceed through two successive stages,¹⁸ and the latter step represents a first example that enol silyl ethers react with alkyl ether moieties.²² A close situation between a benzylic ether and an enol silyl ether moiety may be responsible for such a characteristic transformation.

An acetylenecarboxylic ester undergoes a similar addition of these copper homoenolates to give the corresponding 6-siloxy-2,5-dienoic ester **10**, which serves for preparation of cyclopropyl ketones such as **11** via internal Michael addition mediated by fluoride. However, in contrast to the usual copper species²³, these copper homoenolates do not add to alkynes.

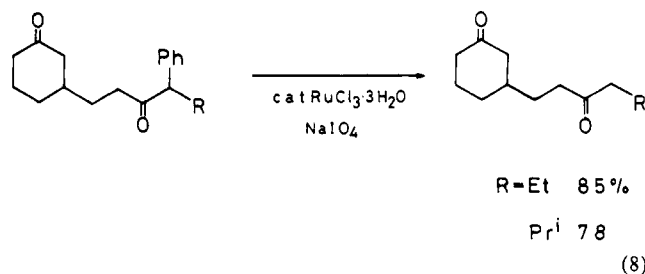
Oxiranes also react to afford the corresponding ring-opening compounds²⁴ in good yield. It should be noted that only copper



trimethylsilylacetylide has proved to be very efficient in this reaction too.



As described above, there is a severe structural limitation on using magnesium homoenolates irrespective of a simple procedure for their generation. To extend the synthetic utility of such nucleophilic species, several efforts have been made, and such a drawback has been partially overcome by using an appropriate 2-phenylacetyltrimethylsilane as follows. Thus, after conjugate addition of some phenyl-substituted ones, the phenyl group can be removed effectively by treating with ruthenium chloride and sodium periodate,²⁵ which involves the oxidation of benzene ring to the carboxylic acid followed by decarboxylation of the resulting β -keto acid.



The regiochemical outcome on 1,2-addition of **1** ($M = \text{MgBr}$, $R' = \text{CH}_3$) was also briefly examined. As expected, these reagents react with ketones at their α -position predominantly, and with acyl chlorides at their α -position exclusively. Thus, in contrast to alkylation⁸ or conjugate addition, **1** does not behave as a homoenolate equivalent in this type of reaction.

Conclusion

It has been shown that an appropriate choice of substrates allows shift of the equilibrium **A** to the electronically much disfavored carbanionic species through the Brook–West rearrangement of a silyl group from carbon to oxide anion. For such purpose, introduction of steric factors either on main chains of alcohols or on a silicon atom is very important, and synthetically attractive nucleophilic species can be generated either as the magnesium or lithium homoenolate equivalent **1**. In addition to their behavior as homoenolate nucleophiles, these reagents **1** can also be used, after appropriate synthetic procedures, as enolate equivalents by taking advantages of their enol silyl ether moieties. Based on such

(18) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011.

(19) Mitra, A. "The Synthesis of Prostaglandins"; Wiley: New York, 1977.

(20) On treatment with Pd(II) or acetals in the presence of TiCl_4 , reactions took place on both trimethylsilyl and *tert*-butyldimethylsilyl enol ether moieties and any regioselectivity was not observed.

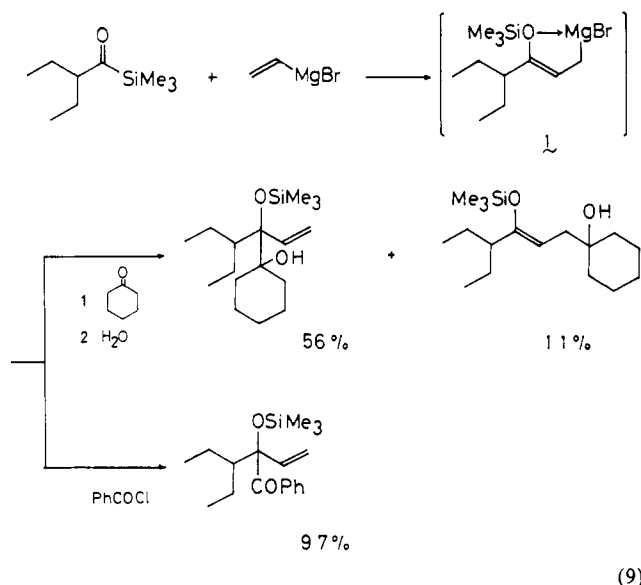
(21) Mukaiyama, T. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 817.

(22) TiCl_4 -mediated reaction of enol silyl ethers with *tert*-alkyl halides: Reetz, M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 96.

(23) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841. Normant, J. F.; Alexakis, A. "Current Trends in Organic Synthesis"; Nozaki, H., Ed.; Pergamon Press: New York, 1983; pp 291–302.

(24) Posner, G. H. *Org. React.* **1975**, *22*, 253.

(25) Carlson, P. H. J.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem.* **1981**, *46*, 3936.



features, two types of different electrophiles or functional groups can be introduced successively on their vicinal carbons, which may further broaden the synthetic utility of these homoenolate equivalents **1**.

Experimental Section

General Procedures. Boiling points are uncorrected. Infrared (IR) spectra were taken on a Hitachi 260-10 spectrometer; absorptions are given in reciprocal centimeters. Proton nuclear magnetic resonance spectra (^1H NMR) were recorded on a Hitachi R-24B spectrometer; chemical shifts (δ) are expressed in parts per million downfield from internal tetramethylsilane. Mass spectra were measured on Hitachi RMU-7M at 20 eV ionizing irradiation. Analytical gas-liquid chromatography (GLC) was performed on a Hitachi 163 instrument with a flame ionization detector and nitrogen carrier gas, using a OV-101 fused silica 20-m capillary column. Microanalyses were performed with a Perkin-Elmer 240 at the Microanalytical Laboratory, Tokyo Institute of Technology.

All the reactions were carried out in a sealed glass tube with a magnetic stirring bar under nitrogen. Column chromatography was performed on Wakogel C-200. Analytical samples were prepared by bulb-to-bulb distillation with a Büchi kugelrohr apparatus.

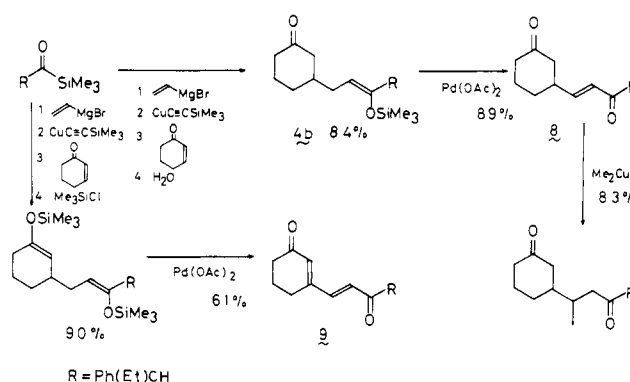
Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl in a recycling still immediately before use. Hexane was used after drying on molecular sieves 3A.

Materials. Acyltrimethylsilanes were prepared from the corresponding trimethylsilyl enol ethers of benzenethiol esters according to the procedure developed in our laboratory.⁹ Acyl(*tert*-butyl)dimethylsilanes were prepared by a slightly modified method.^{9,10}

2-Ethylbutyltrimethylsilane: IR (neat) 1620, 1240, 830; NMR (CCl_4) 0.05 (s, 9 H), 0.70 (t, $J = 7$ Hz, 6 H), 1.27 (m, 4 H), 2.50 (m, 1 H). **2-Phenylbutyltrimethylsilane:** bp 93 °C (bath temperature) (1.9 mmHg); IR (neat) 1630, 1240, 830; NMR (CCl_4) 0.12 (s, 9 H), 0.94 (t, $J = 7$ Hz, 3 H), 1.90 (m, 2H), 3.86 (t, $J = 7$ Hz, 1 H), 7.22 (s, 5 H). Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{OSi}$: C, 70.85; H, 9.15. Found: C, 70.61; H, 8.96. **2-Phenyl-3-methylbutyltrimethylsilane:** bp 99 °C (bath temperature) (1.9 mmHg); IR (neat) 1640, 1240, 830; NMR (CCl_4) 0.24 (s, 9 H), 0.85 (d, $J = 7$ Hz, 3 H), 1.13 (d, $J = 7$ Hz, 3 H), 2.64 (m, 1 H), 3.82 (d, $J = 8$ Hz, 1 H), 7.22 (s, 5 H). Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{OSi}$: C, 71.73; H, 9.46. Found: C, 71.80; H, 9.51. **Acetyl(*tert*-butyl)dimethylsilane:** bp 80 °C (62 mmHg); IR (neat) 1630, 1240, 840; NMR (CCl_4) 0.28 (s, 6 H), 1.02 (s, 9 H), 2.32 (s, 3 H). ***tert*-Butyldimethylpropionylsilane:** bp 83 °C (53 mmHg); IR (neat) 1630, 1240, 840; NMR (CCl_4) 0.25 (s, 9 H), 0.94 (s, 9 H, and t, $J = 7$ Hz, 3 H), 2.64 (q, $J = 7$ Hz, 2 H). ***tert*-Butyldimethyloctanoylsilane:** bp 75 °C (18 mmHg); IR (neat) 1630, 1250, 835; NMR (CCl_4) 0.21 (s, 6 H), 1.01 (s, 9 H, and t, $J = 7$ Hz, 3 H), 1.20–1.69 (m, 10 H), 2.56 (t, $J = 7$ Hz, 2 H). Anal. Calcd for $\text{C}_{14}\text{H}_{30}\text{OSi}$: C, 69.35; H, 12.47. Found: C, 69.20; H, 12.40.

Preparation of 1-(*tert*-Butyldimethylsilyl)allylic Alcohols. An acyl(*tert*-butyl)dimethylsilane (0.4 mmol) was added dropwise to vinylmagnesium bromide (0.5 mL of a 1.0 M THF solution) diluted with ether (1 mL) and the mixture was stirred for 1 h at 0 °C. The resulting solution was quenched with 1 N HCl and the aqueous layer was extracted with hexane. The combined extracts were washed with saturated aqueous NaCl solution and dried over anhydrous MgSO_4 . Removal of the sol-

Scheme I



vents followed by distillation gave the corresponding title compound in almost quantitative yield.

2-(*tert*-Butyldimethylsilyl)-3-buten-2-ol: bp 85 °C (50 mmHg); IR (neat) 3300, 1600, 1240, 840; NMR (CCl_4) 0.20 (s, 6 H), 1.00 (s, 9 H), 1.40 (s, 3 H), 5.11 (dd, $J = 17$ and 2 Hz, 1 H), 5.13 (dd, $J = 10$ and 2 Hz, 1 H), 5.91 (dd, $J = 17$ and 10 Hz, 1 H); mass spectrum m/e (relative %), 186 (M^+ , 0.5), 185 (0.2), 129 (16), 91 (28), 76 (8), 75 (100), 73 (31), 57 (7), 42 (7). **3-(*tert*-Butyldimethylsilyl)-1-penten-3-ol:** bp 103 °C (73 mmHg); IR (neat) 3300, 1600, 1240, 840; NMR (CCl_4) 0.12 (s, 6 H), 1.07 (s, 9 H and t, $J = 7$ Hz, 3 H), 1.32 (q, $J = 7$ Hz, 2 H), 5.15 (dd, $J = 17$ and 2 Hz, 1 H), 5.17 (dd, $J = 10$ and 2 Hz, 1 H), 5.75 (dd, $J = 17$ and 10 Hz, 1 H); mass spectrum m/e (relative %) 200 (M^+ , 0.2), 199 (0.4), 143 (30), 115 (7), 75 (100), 73 (61), 57 (5), 42 (6). **3-(*tert*-Butyldimethylsilyl)-1-decen-3-ol:** bp 100–105 °C (bath temperature) (2.2 mmHg); IR (neat) 3350, 1600, 1240, 840; NMR (CCl_4) 0.17 (s, 6 H), 1.04 (s, 9 H and t, $J = 7$ Hz, 3 H), 1.30–1.60 (m, 12 H), 5.11 (dd, $J = 17$ and 2 Hz, 1 H), 5.13 (dd, $J = 10$ and 2 Hz, 1 H), 5.80 (dd, $J = 17$ and 10 Hz, 1 H); mass spectrum m/e (relative %) 270 (M^+ , 0.2), 269 (0.2), 213 (1), 75 (100), 73 (54), 28 (100).

Generation of a 3-Substituted 3-(Trimethylsiloxy)allylmagnesium Bromide and Its Conjugate Addition Reaction to an α,β -Unsaturated Carbonyl Compound. A General Procedure. An appropriate 2-substituted acyltrimethylsilane (0.1 mmol) in THF (0.4 mL) was added to a THF solution of vinylmagnesium bromide (0.1 mL of 1.0 M solution, 0.1 mmol) at 0 °C and was stirred for 10 min at room temperature. To an ethereal solution (1.5 mL) of copper(I) trimethylsilylacetylide [prepared from lithium trimethylsilylacetylide (0.12 mmol) and cuprous bromide-dimethyl sulfide (0.12 mmol)] was added the resulting solution at –20 °C and the mixture was stirred for 20 min at that temperature. Then an ether (0.1 mL) solution of α,β -unsaturated carbonyl compound (0.1 mmol) was added, and the mixture was further stirred for 2–12 h at –20 °C. The reaction mixture was quenched with aqueous THF (THF/ $\text{H}_2\text{O} = 9:1$) and extracted with hexane. After drying over anhydrous MgSO_4 , removal of the solvents from the combined extracts followed by separation with column chromatography afforded the corresponding monosilyl enol ether of 1,6-dicarbonyl compound **4**.

1-(3-Oxocyclohexyl)-4-ethyl-3-(trimethylsiloxy)-2-hexene (4a): IR (neat) 1700, 1660, 1240, 840; NMR (CCl_4) 0.10 (s, 9 H), 0.70 (t, $J = 7$ Hz, 6 H), 1.05–1.95 (m, 12 H), 2.20–2.35 (m, 4 H), 4.30 (t, $J = 7$ Hz, 1 H). **1-(3-Oxocyclohexyl)-4-phenyl-3-(trimethylsiloxy)-2-hexene (4b):** bp 134 °C (bath temperature) (0.1 mmHg); IR (neat) 1700, 1660, 1250, 830; NMR (CCl_4) 0.22 (s, 9 H), 0.82 (t, $J = 7$ Hz, 3 H), 1.79–2.18 (m, 9 H), 2.47 (m, 4 H), 3.04 (m, 1 H), 4.72 (t, $J = 7$ Hz, 1 H), 7.29 (s, 5 H). Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{O}_2\text{Si}$: C, 73.20; H, 9.36. Found: C, 73.10; H, 9.10. **1-(3-Oxocyclohexyl)-5-methyl-4-phenyl-3-(trimethylsiloxy)-2-hexene (4c):** IR (neat) 1700, 1660, 1240, 840; NMR (CCl_4) 0.23 (s, 9 H), 0.85 (d, $J = 7$ Hz, 6 H), 1.75–2.13 (m, 8 H), 2.40–2.52 (m, 4 H), 3.09 (m, 1 H), 4.70 (t, $J = 7$ Hz, 1 H), 7.23 (s, 5 H). An acidic treatment of this compound afforded 1-(3-oxocyclohexyl)-4-phenyl-5-methyl-3-hexanone: bp 125 °C (bath temperature) (0.9 mmHg); IR (neat) 1700; NMR (CCl_4) 0.74 (d, $J = 6$ Hz, 3 H), 1.04 (d, $J = 6$ Hz, 3 H), 1.35–1.94 (m, 8 H), 2.12–2.55 (m, 6 H), 3.32 (d, $J = 8$ Hz, 1 H), 7.24 (s, 5 H). Anal. Calcd for $\text{C}_{19}\text{H}_{26}\text{O}_2$: C, 79.68; H, 9.15. Found: C, 79.40; H, 9.24. **1-(1-Methyl-3-oxocyclohexyl)-4-phenyl-3-(trimethylsiloxy)-2-hexene (4d):** NMR (CCl_4) 0.22 (s, 9 H), 0.82 (t, $J = 7$ Hz, 3 H), 1.25 (s, 3 H), 1.79–2.18 (m, 8 H), 2.47 (m, 4 H), 3.04 (m, 1 H), 4.72 (t, $J = 7$ Hz, 1 H), 7.29 (s, 5 H). An acidic treatment of this compound gave 1-(1-methyl-3-oxocyclohexyl)-4-phenyl-3-hexanone: bp 151 °C (bath temperature) (0.7 mmHg); IR (neat) 1700; NMR (CCl_4) 0.85 (t, $J = 7$ Hz, 3 H), 1.15 (s, 3 H), 1.30–1.95 (m, 8 H), 2.21–2.59 (m, 6 H), 3.35 (t, $J = 8$ Hz, 1 H), 7.29 (s, 5 H). Anal. Calcd for $\text{C}_{19}\text{H}_{26}\text{O}_2$: C, 79.68; H, 9.15. Found: C, 80.09; H, 9.21. **1-(1-**

Methyl-3-oxocyclohexyl)-5-methyl-4-phenyl-3-(trimethylsiloxy)-2-hexene (4e): IR (neat) 1700, 1660, 1240, 830; NMR (CCl_4) 0.22 (s, 9 H), 0.84 (d, $J = 7$ Hz, 6 H), 1.05 (s, 3 H), 1.69–2.10 (m, 7 H), 2.45 (m, 4 H), 3.10 (m, 1 H), 4.73 (t, $J = 7$ Hz, 1 H), 7.26 (s, 5 H). **8-Phenyl-4-propyl-7-(trimethylsiloxy)-6-decen-2-one (4f):** NMR (CCl_4) 0.22 (s, 9 H), 1.07 (t, $J = 7$ Hz, 3 H), 1.37–1.61 (m, 7 H), 1.91 (m, 2 H), 2.20 (s, 3 H), 2.45 (m, 2 H), 3.03 (t, $J = 7$ Hz, 1 H), 4.71 (m, 1 H), 7.33 (s, 5 H). An acidic treatment of this compound afforded 8-phenyl-4-propyl-2,7-decanedione: bp 137 °C (bath temperature) (0.7 mmHg); IR (neat) 1700; NMR (CCl_4) 0.85 (t, $J = 7$ Hz, 6 H), 1.29–1.84 (m, 9 H), 2.05 (s, 3 H), 2.22–2.45 (m, 4 H), 3.33 (t, $J = 8$ Hz, 1 H), 7.23 (s, 5 H). Anal. Calcd for $\text{C}_{19}\text{H}_{28}\text{O}_2$: C, 79.12; H, 9.79. Found: C, 78.98; H, 9.88. **9-Methyl-8-phenyl-4-propyl-7-(trimethylsiloxy)-6-decen-2-one (4g):** IR (neat) 1700, 1660, 1240, 840; NMR (CCl_4) 0.22 (s, 9 H), 0.85 (d, $J = 7$ Hz, 6 H), 1.05 (t, $J = 7$ Hz, 3 H), 1.30–1.58 (m, 6 H), 1.89 (m, 2 H), 2.22 (s, 3 H), 2.45 (m, 2 H), 3.05 (t, $J = 7$ Hz, 1 H), 4.72 (m, 1 H), 7.30 (s, 5 H). An acidic treatment of this compound afforded 9-methyl-8-phenyl-4-propyl-2,7-decanedione: bp 131 °C (bath temperature) (0.8 mmHg); IR (neat) 1700; NMR (CCl_4) 0.73 (d, $J = 6$ Hz, 3 H), 1.01 (d, $J = 6$ Hz, 3 H), 1.29–1.88 (m, 8 H), 2.18 (s, 3 H), 2.22–2.49 (m, 4 H), 3.35 (d, $J = 8$ Hz, 1 H), 7.28 (s, 5 H). Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{O}_2$: C, 79.42; H, 10.00. Found: C, 79.59; H, 9.94. **7-Phenyl-3-propyl-6-(trimethylsiloxy)-5-nonenal (4h):** IR (neat) 2700, 1720, 1660, 1250, 840; NMR (CCl_4) 0.24 (s, 9 H), 1.04 (t, $J = 7$ Hz, 3 H), 1.09 (t, $J = 7$ Hz, 3 H), 1.46 (m, 7 H), 1.87 (m, 2 H), 2.45 (m, 2 H), 3.63 (t, $J = 7$ Hz, 1 H), 4.66 (m, 1 H), 7.27 (s, 5 H), 9.79 (t, $J = 2$ Hz, 1 H). **Ethyl 7-Phenyl-6-(trimethylsiloxy)-5-nonenate (4i):** IR (neat) 1720, 1650, 1250, 840; NMR (CCl_4) 0.14 (s, 9 H), 0.95 (t, $J = 7$ Hz, 6 H), 1.36 (m, 4 H), 1.95 (m, 2 H), 2.50 (t, $J = 7$ Hz, 2 H), 3.49 (t, $J = 8$ Hz, 1 H), 4.21 (q, $J = 7$ Hz, 2 H), 4.66 (t, $J = 7$ Hz, 1 H), 7.23 (s, 5 H). **Ethyl 7-Phenyl-3-propyl-6-(trimethylsiloxy)-5-nonenate (4j):** IR (neat) 1720, 1660, 1250, 840; NMR (CCl_4) 0.24 (s, 9 H), 1.00 (t, $J = 7$ Hz, 6 H), 1.02 (t, $J = 7$ Hz, 3 H), 1.34–1.76 (m, 7 H), 1.90 (m, 2 H), 2.45 (m, 2 H), 3.40 (t, $J = 8$ Hz, 1 H), 4.21 (q, $J = 7$ Hz, 2 H), 4.69 (t, $J = 7$ Hz, 1 H), 7.29 (s, 5 H).

By the same procedure, 4-phenyl-3-(trimethylsiloxy)-2-hexenyl-magnesium bromide reacted with 1-hexene oxide to give **10-phenyl-9-(trimethylsiloxy)-8-dodecen-5-ol**: bp 121 °C (bath temperature) (0.9 mmHg); IR (neat) 3300, 1240, 840; NMR (CCl_4) 0.09 (s, 9 H), 0.92 (t, $J = 7$ Hz, 3 H), 1.37–1.47 (m, 10 H), 2.17 (m, 2 H), 2.78 (t, $J = 7$ Hz, 1 H), 3.46 (m, 1 H), 4.54 (m, 1 H), 7.20 (s, 5 H). Anal. Calcd for $\text{C}_{21}\text{H}_{36}\text{O}_2\text{Si}$: C, 72.35; H, 10.41. Found: C, 72.42; H, 10.38.

Conjugate Addition Reaction of a 3-(tert-Butyldimethylsilyl)allyllithium to an α,β -Unsaturated Carbonyl Compound. General Procedure A. A hexane (0.1 mL) solution of 1-(tert-butyldimethylsilyl)allylic alcohol (0.1 mmol) was added to butyllithium (0.26 mL of 1.6 M hexane solution, 0.1 mmol) at -70 °C and the solution was stirred for 20 min at that temperature. THF (0.4 mL) was then slowly added and the resulting solution was stirred for 1 h at that temperature. An ether (1.5 mL) solution of copper(I) trimethylsilylacetylide (0.12 mmol) was added to the resulting solution and the mixture was stirred for 20 min at the same temperature. An ether (0.1 mL) solution of an enone (0.1 mmol) was added and was stirred for 3 h at -70 °C. The reaction mixture was quenched with aqueous THF (THF/ $\text{H}_2\text{O} = 9:1$) and extracted with hexane. After drying over anhydrous MgSO_4 , removal of the solvents followed by purification with column chromatography gave the corresponding monosilyl enol ether of 1,6-dicarbonyl compound 6.

3-[3-(tert-Butyldimethylsilyloxy)-2-pentenyl]cyclohexanone (6b): IR (neat) 1700, 1660, 1240, 840; NMR (CCl_4) 0.13 (s, 6 H), 1.01 (s, 9 H and t, $J = 7$ Hz, 3 H), 1.29–1.59 (m, 5 H), 1.99 (m, 4 H), 2.16 (m, 4 H), 4.46 (t, $J = 7$ Hz, 1 H). **1-(3-Oxocyclohexyl)-3-(tert-butyldimethylsilyloxy)-2-decene (6c):** bp 150 °C (bath temperature) (0.05 mmHg); IR (neat) 1700, 1660, 1240, 840; NMR (CCl_4) 0.12 (s, 6 H), 0.97 (s, 9 H and t, $J = 7$ Hz, 3 H), 1.20–1.46 (m, 15 H), 2.01 (m, 4 H), 2.18 (m, 4 H), 4.44 (t, $J = 7$ Hz, 1 H). Anal. Calcd for $\text{C}_{22}\text{H}_{42}\text{O}_2\text{Si}$: C, 72.07; H, 11.55. Found: C, 72.27; H, 11.27. **7-(tert-Butyldimethylsilyloxy)-6-tetradecen-2-one (6f):** bp 100 °C (bath temperature) (1.0 mmHg); IR (neat) 1700, 1660; NMR (CCl_4) 0.22 (s, 6 H), 1.08 (t, $J = 7$ Hz, 3 H), 1.25–1.55 (m, 12 H), 1.83 (t, $J = 7$ Hz, 2 H), 2.06 (m, 2 H), 2.21 (s, 3 H), 2.78 (t, $J = 7$ Hz, 2 H), 4.41 (t, $J = 7$ Hz, 1 H). Anal. Calcd for $\text{C}_{20}\text{H}_{40}\text{O}_2\text{Si}$: C, 70.52; H, 11.84. Found: C, 70.73; H, 11.70.

By similar procedure, 3-(tert-butyldimethylsilyloxy)-2-decenyllithium reacts with octene 1-oxide or methyl propiolate to give the corresponding ring-opening or addition product. **11-(tert-Butyldimethylsilyloxy)-10-oc-tadecen-7-ol**: IR (neat) 3300, 1240, 830; NMR (CCl_4) 0.21 (s, 6 H), 0.98 (s, 9 H and t, $J = 7$ Hz, 3 H), 1.26–1.56 (m, 22 H), 1.81 (t, $J = 7$ Hz, 2 H), 2.18 (m, 2 H), 3.60 (m, 1 H), 4.47 (t, $J = 7$ Hz, 1 H). **Methyl 6-(tert-Butyldimethylsilyloxy)-2,5-tridecadienoate (10):** bp 82 °C (bath temperature) (0.25 mmHg); IR (neat) 1700, 1660, 1240, 830;

NMR (CCl_4) 0.07 (s, 6 H), 0.90 (s, 9 H and t, $J = 7$ Hz, 3 H), 1.18–1.37 (m, 10 H), 1.94 (m, 2 H), 2.81 (dd, $J = 7$ and 6 Hz, 2 H), 3.58 (s, 3 H), 4.32 (t, $J = 7$ Hz, 1 H), 5.71 (d, $J = 16$ Hz, 1 H), 6.70 (dt, $J = 16$ and 6 Hz, 1 H).

Conjugate Addition of a 3-(tert-Butyldimethylsilyloxy)allyllithium to an α,β -Unsaturated Carbonyl Compound. General Procedure B. An appropriate 3-(tert-butyldimethylsilyloxy)allyllithium (0.1 mmol) was treated with copper(I) trimethylsilylacetylide (0.12 mmol) as described above. To the resulting solution was added an ether (0.1 mL) solution of an enone (0.1 mmol), triethylamine (0.2 mmol), and chlorotrimethylsilane (0.2 mmol), and the mixture was stirred for 2 h at -70 °C. Then the reaction mixture was diluted with hexane and filtered. Removal of the solvents followed by silica gel column chromatography gave the corresponding bis-silyl enol ether 7.

3-[3-(tert-Butyldimethylsilyloxy)-2-butenyl]-1-(trimethylsilyloxy)-1-cyclohexene (7a): IR (neat) 1660, 1240, 830; NMR (CCl_4) 0.17 (s, 6 H), 0.22 (s, 9 H), 1.10 (s, 9 H), 1.42 (m, 4 H), 1.79 (m, 3 H), 1.81 (s, 3 H), 1.88 (m, 2 H), 4.58 (t, $J = 7$ Hz, 1 H), 4.90 (m, 1 H). **3-[3-(tert-Butyldimethylsilyloxy)-2-pentenyl]-1-(trimethylsilyloxy)-1-cyclohexene (7b):** bp 110 °C (bath temperature) (32 mmHg); IR (neat) 1660, 1240, 840; NMR (CCl_4) 0.29 (s, 15 H), 1.00 (s, 9 H), 1.09 (t, $J = 7$ Hz, 3 H), 1.38 (m, 4 H), 1.66 (m, 3 H), 1.98 (m, 4 H), 4.48 (t, $J = 8$ Hz, 1 H), 4.85 (m, 1 H). Anal. Calcd for $\text{C}_{20}\text{H}_{40}\text{O}_2\text{Si}_2$: C, 65.15; H, 10.94. Found: C, 65.13; H, 10.65. **3-[3-(tert-Butyldimethylsilyloxy)-1-3-(trimethylsilyloxy)-2-cyclohexenyl]-2-decene (7c):** IR (neat) 1660, 1240, 840; NMR (CCl_4) 0.13 (s, 6 H), 0.20 (s, 9 H), 0.97 (s, 9 H and t, $J = 7$ Hz, 3 H), 1.15–1.39 (m, 14 H), 1.63 (m, 3 H), 2.02 (m, 4 H), 4.46 (t, $J = 7$ Hz, 1 H), 4.83 (m, 1 H). **3-[3-(tert-Butyldimethylsilyloxy)-2-pentenyl]-3-methyl-1-(trimethylsilyloxy)-1-cyclohexene (7d):** bp 103 °C (bath temperature) (31 mmHg); IR (neat) 1660, 1240, 840; NMR (CCl_4) 0.28 (s, 15 H), 1.03 (s, 9 H and t, $J = 7$ Hz, 3 H), 1.33 (m, 4 H), 1.68 (m, 2 H), 1.94 (m, 4 H), 4.48 (m, 1 H), 4.70 (m, 1 H). Anal. Calcd for $\text{C}_{21}\text{H}_{42}\text{O}_2\text{Si}_2$: C, 65.90; H, 11.06. Found: C, 66.12; H, 10.80. **3-(tert-Butyldimethylsilyloxy)-1-[1-methyl-3-(trimethylsilyloxy)-2-cyclohexenyl]-2-decene (7e):** bp 120 °C (bath temperature) (2.8 mmHg); IR (neat) 1660, 1240, 840; NMR (CCl_4) 0.21 (s, 6 H), 0.27 (s, 9 H), 1.06 (s, 9 H and t, $J = 7$ Hz, 3 H), 1.23–1.48 (m, 14 H), 1.65 (m, 2 H), 2.04 (m, 4 H), 4.50 (t, $J = 7$ Hz, 1 H), 4.73 (m, 1 H). Anal. Calcd for $\text{C}_{26}\text{H}_{52}\text{O}_2\text{Si}_2$: C, 68.96; H, 11.57. Found: C, 68.84; H, 11.84. **7-(tert-Butyldimethylsilyloxy)-4-propyl-2-(trimethylsilyloxy)-2,6-nonadiene (7g):** bp 89 °C (bath temperature) (16 mmHg); IR (neat) 1660, 1240, 840; NMR (CCl_4) 0.28 (s, 15 H), 0.98 (s, 9 H and t, $J = 7$ Hz, 3 H), 1.33 (m, 4 H), 1.60 (s, 3 H), 1.80 (m, 4 H), 1.87 (m, 1 H), 4.31 (m, 2 H). Anal. Calcd for $\text{C}_{21}\text{H}_{44}\text{O}_2\text{Si}_2$: C, 65.56; H, 11.52. Found: C, 65.72; H, 11.20. **7-(tert-Butyldimethylsilyloxy)-4-propyl-2-(trimethylsilyloxy)-2,6-tetradecadiene (7h):** bp 103 °C (bath temperature) (0.5 mmHg); IR (neat) 1660, 1240, 840; NMR (CCl_4) 0.12 (s, 6 H), 0.23 (s, 9 H), 1.07 (s, 9 H and t, $J = 7$ Hz, 6 H), 1.24–1.50 (m, 14 H), 1.65 (s, 3 H), 1.99 (m, 4 H), 2.04 (m, 1 H), 4.51 (m, 2 H). Anal. Calcd for $\text{C}_{26}\text{H}_{54}\text{O}_2\text{Si}_2$: C, 68.65; H, 11.97. Found: C, 68.80; H, 11.89.

Conversion of 1-(3-Oxocyclohexyl)-4-phenyl-3-(trimethylsilyloxy)-2-hexene to 1-(3-Oxocyclohexyl)-4-phenyl-1-hexen-3-one (8). A mixture of the title silyl enol ether (0.05 mmol) and palladium acetate (0.05 mmol) was stirred in acetonitrile (0.1 mL) for 6 h at room temperature. The reaction mixture was diluted with ether and filtered. Removal of the solvents followed by purification with silica gel column chromatography gave **1-(3-oxocyclohexyl)-4-phenyl-1-hexen-3-one (8)** (90%): bp 130 °C (bath temperature) (0.9 mmHg); IR (neat) 1700, 1660, 1620; NMR (CCl_4) 0.89 (t, $J = 7$ Hz, 3 H), 1.78–2.19 (m, 6 H), 2.34 (m, 5 H), 3.60 (m, 1 H), 6.12 (d, $J = 15$ Hz, 1 H), 6.55 (dd, $J = 15$ and 6 Hz, 1 H), 7.18 (s, 5 H).

By a similar procedure, a bis-silyl enol ether gave the corresponding dienone, **1-(3-oxo-1-cyclohexenyl)-4-phenyl-1-penten-3-one (9)**: IR (neat) 1660, 1600; NMR (CCl_4) 1.00 (t, $J = 7$ Hz, 3 H), 1.40 (m, 2 H), 2.20 (m, 2 H), 2.42 (m, 2 H), 2.80 (m, 2 H), 3.84 (t, $J = 7$ Hz, 1 H), 6.20 (s, 1 H), 6.58 (d, $J = 16$ Hz, 1 H), 7.20 (d, $J = 16$ Hz, 1 H), 7.25 (s, 5 H).

Conjugate Addition of Lithium Dimethylcuprate to 1-(3-Oxocyclohexyl)-4-phenyl-1-hexen-3-one (8). To lithium dimethylcuprate (0.06 mmol) in ether (0.2 mL) was added the title enedione **8** (0.05 mmol) in ether (0.2 mL) at -40 °C, and the mixture was stirred for 4 h at that temperature. Then the solution was quenched with saturated aqueous NH_4Cl solution and the aqueous layer was extracted with ether. After drying over anhydrous MgSO_4 , removal of the solvents followed by purification with silica gel column chromatography gave **2-(3-oxocyclohexyl)-5-phenyl-4-heptanone (83%)**: IR (neat) 1700; NMR (CCl_4) 0.90 (t, $J = 7$ Hz, 3 H), 1.36 (d, $J = 4$ Hz, 3 H), 1.88–2.10 (m, 8 H), 2.29–2.35 (m, 6 H), 3.35 (d, $J = 8$ Hz, 1 H), 7.22 (s, 5 H).

Oxidative Removal of a Phenyl Group from a Benzyl Diketone with Ruthenium Tetroxide. A General Procedure. A mixture of a benzyl

ketone (0.03 mmol), NaIO_4 (0.75 mmol), and $\text{RuCl}_3(\text{H}_2\text{O})_3$ (0.002 mmol) was stirred in $\text{CCl}_4\text{-H}_2\text{O-CH}_3\text{CN}$ (2:1:2) (1.0 mL) for 36-48 h at room temperature. The resulting mixture was diluted with ether and the organic layer was dried over anhydrous MgSO_4 . Removal of the solvents followed by separation with column chromatography gave the corresponding diketone. **1-(3-Oxocyclohexyl)-3-hexanone**: bp 145 °C (bath temperature) (20 mmHg); IR (neat) 1700; NMR (CCl_4) 0.85 (t, $J = 7$ Hz, 3 H), 1.31-2.08 (m, 9 H), 2.33 (m, 8 H). **1-(3-Oxocyclohexyl)-5-methyl-3-hexanone**: bp 150 °C (bath temperature) (20 mmHg); IR (neat) 1700; NMR (CCl_4) 0.98 (d, $J = 7$ Hz, 6 H), 1.33-1.66 (m, 8 H), 2.31 (m, 8 H).

Lewis Acid Mediated Reaction of Bis-Silyl Enol Ether 7c with an Aromatic Acetal. To a dichloromethane (0.2 mL) solution of an aromatic acetal (0.08 mmol) and SnCl_4 (0.08 mmol) was added a dichloromethane (0.1 mL) solution of 3-(*tert*-butyldimethylsiloxy)-1-[3-(trimethylsiloxy)-2-cyclohexenyl]-2-decene (**7c**) (0.08 mmol) at -70 °C and the mixture was stirred for 1 h at that temperature. Then the reaction mixture was quenched with saturated aqueous NaHCO_3 solution and the aqueous layer was extracted with ether. The combined extracts were washed with saturated aqueous NaCl solution and dried over anhydrous MgSO_4 . Removal of the solvents followed by separation with silica gel column chromatography afforded the corresponding ring-closure product.

2-(1-Octanoyl)-3-phenyl-4,5,6,7-tetrahydro-4-indanone: yield 65%; IR (neat) 1700; NMR (CCl_4) 0.82 (t, $J = 7$ Hz, 3 H), 1.12-1.43 (m, 17 H), 1.59 (m, 1 H), 1.89-2.43 (m, 6 H), 7.12-7.16 (m, 5 H). **2-(1-Octanoyl)-3-ethyl-3-phenyl-4,5,6,7-tetrahydro-4-indanone**: yield 62%; IR (neat) 1700; NMR (CCl_4) 0.89 (t, $J = 7$ Hz, 6 H), 1.10-1.50 (m, 19 H), 1.92-2.47 (m, 6 H), 7.21 (bs, 10 H).

Fluoride-Induced Cyclization of 6-Siloxy-2,5-dienoic Ester 10. A THF (0.1 mL) solution of methyl 6-(*tert*-butyldimethylsiloxy)-2,5-tridecadienoate (**10**) (70.8 mg, 0.25 mmol) was added to a THF (0.2 mL) solution of tetrabutylammonium fluoride (97.9 mg, 0.38 mmol) at -70 °C. After the mixture was stirred for 1 h at -70 °C, for 1 h at -40 °C, and then for 30 min at 0 °C, it was quenched with 1 N HCl. The aqueous layer was extracted with ether and the combined extracts were dried over anhydrous MgSO_4 . Removal of the solvents followed by purification with column chromatography gave 2-(methoxycarbonylmethyl)cyclopropyl heptyl ketone (**11**) (37.2 mg, 62%); IR (neat) 1720, 1700; NMR (CCl_4) 0.90 (t, $J = 7$ Hz, 3 H), 1.10-1.28 (m, 13 H), 1.95-2.10 (m, 5 H), 3.56 (s, 3 H).

Reaction of 4-Ethyl-3-(trimethylsiloxy)-2-hexenylmagnesium Bromide with Cyclohexanone. 2-Ethylbutyryltrimethylsilane (0.1 mmol) was added to a THF solution of vinylmagnesium bromide (0.1 mL of a 1.0 M solution, 0.1 mmol) at 0 °C and the solution was stirred for 10 min at room temperature. To the resulting solution was added a THF (0.2 mL) solution of cyclohexanone (0.1 mmol) at 0 °C and the mixture was stirred for 10 h at room temperature. The solution was then quenched with saturated aqueous NaCl solution and the aqueous layer was extracted with ether. After the combined extracts were dried over anhydrous MgSO_4 , removal of the solvents followed by separation with silica gel column chromatography afforded 1-[3-(4-ethyl-3-trimethylsiloxy-1-hexenyl)]cyclohexan-1-ol (16.6 mg, 56%) and 1-(4-ethyl-3-trimethylsiloxy-2-hexenyl)cyclohexan-1-ol (3.4 mg, 11%). **1-[3-(4-Ethyl-3-trimethylsiloxy-1-hexenyl)]cyclohexan-1-ol**: IR (neat) 3350, 1240, 840; NMR (CCl_4) 0.02 (s, 9 H), 0.73 (t, $J = 7$ Hz, 6 H), 1.09-1.47 (m, 15 H), 4.66 (dd, $J = 17$ and 2 Hz, 1 H), 4.68 (dd, $J = 10$ and 2 Hz, 1 H), 5.38 (dd, $J = 17$ and 10 Hz, 1 H). **1-(4-Ethyl-3-trimethylsiloxy-2-hexenyl)cyclohexan-1-ol**: IR (neat) 3350, 1250, 840; NMR (CCl_4) 0.10 (s, 9 H), 0.77 (t, $J = 7$ Hz, 6 H), 1.13-1.44 (m, 14 H), 1.93 (d, $J = 7$ Hz, 2 H), 2.52 (m, 1 H), 4.28 (t, $J = 7$ Hz, 1 H).

Reaction of 4-Ethyl-3-(trimethylsiloxy)-2-hexenylmagnesium Bromide with Benzoyl Chloride. To a THF solution of the hexenylmagnesium bromide (0.1 mmol) generated as above was added a THF (0.2 mL) solution of benzoyl chloride (0.1 mmol) at -70 °C, and the mixture was stirred for 1 h at -70 °C and then for 1 h at 0 °C. The solution was diluted with ether and quenched with saturated aqueous NaHCO_3 solution. The aqueous layer was extracted with ether and the combined extracts were dried over anhydrous MgSO_4 . Removal of the solvents followed by separation with silica gel column chromatography afforded 3-benzoyl-4-ethyl-3-(trimethylsiloxy)-1-hexene (29.9 mg, 97%); IR (neat) 1690, 1240, 840; NMR (CCl_4) 0.02 (s, 9 H), 0.80 (t, $J = 7$ Hz, 6 H), 1.33-2.27 (m, 5 H), 5.40 (dd, $J = 17$ and 2 Hz, 1 H), 5.42 (dd, $J = 9$ and 2 Hz, 1 H), 5.86 (dd, $J = 17$ and 9 Hz, 1 H), 7.20-7.34 (m, 3 H), 7.61-7.97 (m, 2 H).

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Dimerization of the [8]Annulene Anion Radical

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Abstract: Dilute solutions of the anion radical of [8]annulene ($[\text{8}]^{\cdot-}$) in hexamethylphosphoramide, where ion association is absent, dimerize, resulting in the formation of the [16]annulene anion radical. This disappearance of $[\text{8}]^{\cdot-}$ follows second-order kinetics (rate = $-d[\text{8}]^{\cdot-}/dt = k[\text{8}]^{\cdot-}]^2$) with a rate constant of $7.5 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ at 30 °C. However, the rate of formation of the [16]annulene anion radical is much slower than the rate of disappearance of $[\text{8}]^{\cdot-}$. This is interpreted in terms of a polymerization reaction.

A number of aromatic hydrocarbon cation radicals (R^+) react spontaneously with neutral molecule (R) to form the dimer cation radical (R_2^+).¹ On the other hand, it has been predicted that analogous anion radical dimers ($\text{R}_2^{\cdot-}$) would be unstable relative to the monomer anion radical and neutral molecule.^{2,3} Indeed, hydrocarbon dimer anion radicals have yet to be observed.²

However, Williams and co-workers⁴ did find that a frozen solution of the anion radical of tetrafluoroethylene in methyltetrahydrofuran (MTHF) readily reacts with neutral C_2F_4 to form the anion radical of perfluorocyclobutane. Their work⁴ represents the only documented case for the formation of a dimer anion radical from an olefinic anion radical. The only other dimer anion radicals have been those of the nitriles.⁴ Theory suggests that the forbidden (2 + 2) suprafacial process, which is forbidden for the $\pi\text{-}\pi^*$ cycloaddition of ethylene,⁵ becomes allowed for the Williams

(1) (a) Howarth, O. W.; Fraenkel, G. K. *J. Chem. Phys.* **1970**, *52*, 6258. (b) Lewis, I. C.; Singer, L. S. *Ibid.* **1965**, *43*, 2712. (c) Edlund, O.; Kinell, P. O.; Lund, A.; Shimizu, S. *Ibid.* **1967**, *46*, 3679.

(2) (a) Brocklehurst, B. *J. Phys. Chem.* **1971**, *75*, 1177; (b) Itoh, M. *J. Am. Chem. Soc.* **1970**, *92*, 7239.

(3) Almlof, J.; Lund, A.; Thuomas, K. A. *Chem. Phys. Lett.* **1975**, *32*, 190.

(4) McNeil, R. I.; Shiotani, M.; Williams, F.; Yim, M. B. *Chem. Phys. Lett.* **1977**, *51*, 438.