

The cyclopropane ring asymmetry is consistent with the orientation of the carbomethoxy groups about this ring. π -Electron acceptors are known to affect the geometry of cyclopropanes because of the interaction between the LUMO of the electron acceptor system and the cyclopropane HOMO of the correct symmetry ($3e'$).^{3,14} The resultant transfer of electron density from the cyclopropane to the π -electron acceptor system weakens those bonds for which the $3e'$ orbital is bonding (the vicinal bonds) and strengthens the distal bond (for which the $3e'$ orbital is anti-bonding). The extent of this interaction is dependent on the geometric relationship of the two orbital systems. It can be assessed by measuring the dihedral angle between the carbonyl oxygen and the midpoint of the distal cyclopropane bond (e.g., O8-C14-C8-midpoint C1-C2); at 0° maximum overlap occurs, while at 90° there is no overlap.¹⁴ The data from Table I can be used to calculate the relevant dihedral angles for compound Ib. These angles are 2.95° for the C=O bond to C8 and 115° for the C=O bond to C2. The carbonyl group bound to C2 is twisted almost completely out of conjugation with the Walsh orbitals, while that attached to C8 adopts the most favorable conformation for orbital overlap. Therefore, the C1-C8 bond is lengthened because of the vicinal, interacting carbomethoxy substituent and is not competitively shortened by the C2 carbomethoxy group. Conversely, the C1-C2 bond is shortened as it is distal to the C8 substituent.

Applying this theory to the C2-C8 bond, one would expect a bond length similar to that of C1-C8. A study of a series of substituted cyclopropanes has shown that the bond lengthening induced by a π -electron acceptor need not be equal for both vicinal bonds.¹⁴ However, the effects of these substituents is nowhere near as large as is seen here for the C2-C8 distance. While molecules containing a cyclopropane ring with one long C-C bond are known,^{14,18} there are very few in which the bond distance is greater than 1.6 \AA .¹⁹ The C2-C8 bond length of semibullvalene (Ia) is 1.6 \AA .¹⁶ A steric effect caused by the adjacent carbomethoxy groups might influence the C2-C8 bond length. This is unlikely as identical substitution at the open end of Ib does not increase the C4-C6 distance with respect to the unsubstituted compounds.^{16,17}

It is not possible to draw exact parallels between the crystal and solution structures of Ib since crystal packing may affect the former. However, it appears that the pattern of substitution in Ib has led to a substantial electronic rearrangement as manifested by the unusual crystal structure. The observed geometry is consistent with a structure that is approaching the transition state for Cope rearrangement (IIb). In addition to the extremely long C2-C8 bond, the short nonbonded C4-C6 distance and the long C1-C5 bond (1.581 \AA), the C2-C3 and C7-C8 bonds are significantly shorter than average. Theoretical calculations assessing the effects of both geometry and substituents on the reaction pathway for this Cope rearrangements are in progress.²⁰ These results will be used as guidelines for further synthetic work.

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Supplementary Material Available: Atomic position and thermal parameters for Ib (4 pages). Ordering information is given on any current masthead page.

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α -Silyl Aldehydes: Preparation and Use as Stereoselective Vinyl Cation Equivalents¹

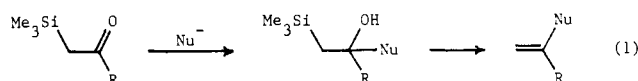
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Efficient methods for the introduction of a vinyl group α to carbonyl would be very desirable not only for the synthesis of biologically important α -vinylcarbonyl compounds but also for the preparation of synthetic intermediates, e.g., substrates for Cope and Claisen rearrangements. A number of vinyl cation equivalents have been recently reported,²⁻⁴ but few have been used with simple ketone enolates.³ We have previously reported the use of α,β -epoxysilanes as stereospecific vinyl cation equivalents for the synthesis of olefins⁵ and heteroatom-substituted olefins.⁶ Attempts to use α,β -epoxysilanes for the preparation of α -vinylcarbonyl compounds, however, have so far been unsuccessful.⁷ We have therefore become interested in the possibility of using α -silyl aldehydes as vinyl cation equivalents.

A number of years ago we⁸ and others⁹ demonstrated that α -trimethylsilyl ketones (β -ketosilanes) could serve as (secondary) vinyl cation equivalents according to eq 1 ($R \neq H$). The pos-



sibility of using α -silyl aldehydes as (primary) vinyl cation equivalents in a similar process (eq 1, $R = H$) was stymied by the lack of methods for preparing α -silyl aldehydes. Our attempts to prepare and isolate simple α -trimethylsilyl aldehydes have been unsuccessful, indicating they are quite sensitive, easily losing silicon (by hydrolysis) or isomerizing to silyl enol ethers,¹⁰ although we¹¹

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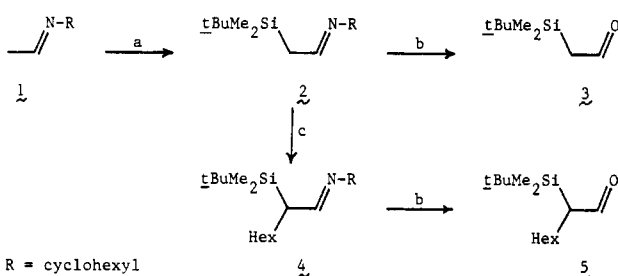
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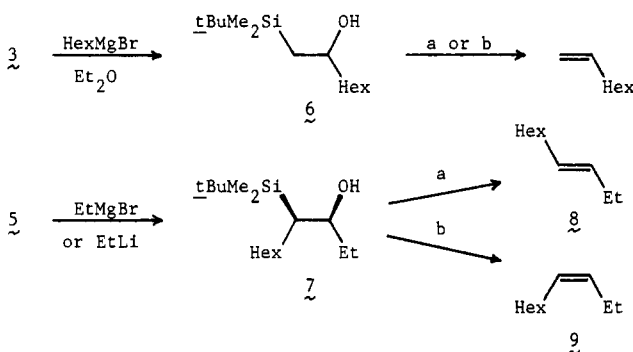
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Scheme I^a

R = cyclohexyl

^a (a) LDA, THF, 0 °C, 15 min; *t*-BuMe₂SiCl, -78 °C, warmed to room temperature. (b) AcOH, H₂O, CH₂Cl₂, room temperature; see ref 16. (c) LDA, THF, -78 °C, 1 h; HexBr, -78 °C, warmed to room temperature.

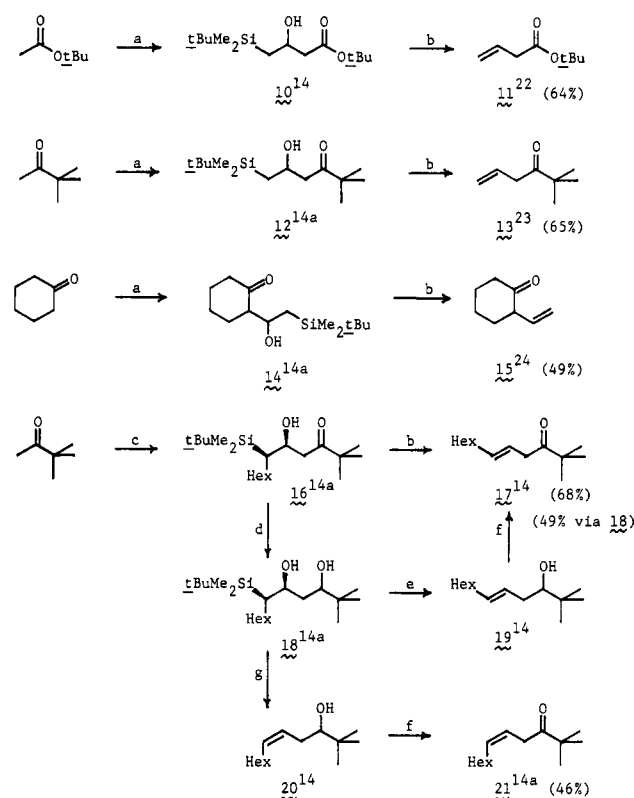
Scheme II^a

conditions for EtM addition to 5 (79–85% yields)	isomeric purity ²¹ of 8 (from BF ₃ ·Et ₂ O) (84–89% yields)	isomeric purity ²¹ of 9 (from KH) (72–79% yields)
EtLi, Et ₂ O, -78 °C	95% trans	94% cis
EtMgBr, Et ₂ O, room temperature	98% trans	97% cis
EtMgBr, Et ₂ O, -78 °C	99.5% trans	99% cis

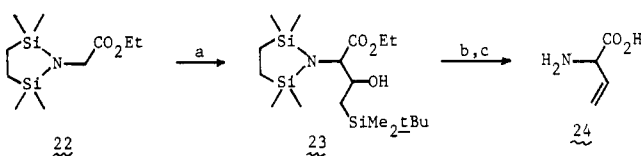
^a (a) BF₃·Et₂O, CH₂Cl₂, room temperature, 1 h. (b) KH, THF, room temperature, 2 h.

and Kuwajima¹² have shown that α -trimethylsilyl aldehydes can be generated and trapped in situ by Grignard reagents.

We now report a potentially general method for preparing α -*tert*-butyldimethylsilyl aldehydes by hydrolysis of the corresponding α -silyl imines and the use of these aldehydes as vinyl cation equivalents. Treatment of the cyclohexylamine imine (1)¹³ of acetaldehyde with lithium diisopropylamide (LDA) followed by *tert*-BuMe₂SiCl produced the α -*tert*-butyldimethylsilyl imine 2^{14a,15} (see Scheme I). Although we have been unable to effect C-silylation of an imine of a long-chain aldehyde (octanal), the desired product (4)^{14a} was prepared by alkylation of 2 with *n*-hexyl

Scheme III^a

^a (a) LDA, THF, -78 °C, 1 h; 3, -78 °C, 30 min. (b) BF₃·Et₂O, CH₂Cl₂, 0 °C, 10–15 min. (c) LDA, Et₂O, -78 °C, 1 h; 5, -78 °C, 4 h. (d) LiAlH₄, Et₂O, room temperature, 2 h. (e) BF₃·Et₂O, CH₂Cl₂, room temperature, 2 h (see ref 25). (f) CrO₃, H₂SO₄, acetone, 10 °C, 5 min. (g) KH, THF, room temperature, 2 h.

Scheme IV^a

^a (a) LDA, THF, -78 °C, 1 h; 3, -78 °C, 1 h. (b) BF₃·Et₂O, CH₂Cl₂, room temperature, 16 h. (c) 6 M HCl reflux, 3 h.

bromide. Careful two-phase hydrolysis of the imines 2 and 4 with aqueous acetic acid and CH₂Cl₂¹⁶ gave the α -silyl aldehydes 3¹⁴ and 5¹⁴ in overall yields (from 1) of 67% and 63%, respectively. [Simple (one-phase) hydrolysis with acetic acid led to *tert*-butyldimethylsilanol (resulting from carbon-silicon bond cleavage) as the predominant product.¹⁷] We have also prepared α -*tri*-methylsilyl imines by procedures analogous to those used above, but attempts to hydrolyze these compounds have so far resulted in carbon-silicon bond cleavage.

α -*tert*-Butyldimethylsilyl aldehydes serve as stereoselective vinyl cation equivalents in their reactions with organometallic reagents (followed by β -elimination reactions of the product β -hydroxy-silanes—Scheme II). Although we were concerned that the β -elimination reactions might not be possible under mild condi-

(10) The existing literature of α -silyl aldehydes is summarized in ref 11b.

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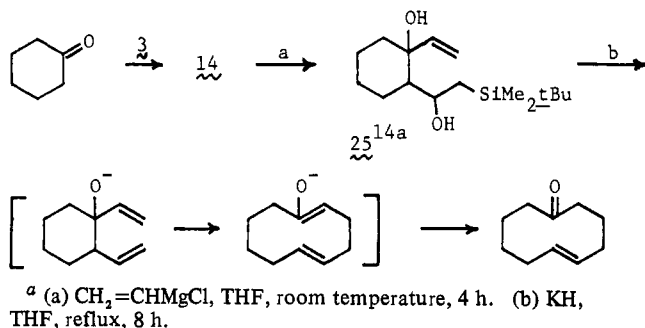
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(15) Although aldehyde and ketone enolates normally undergo exclusive O-silylation, anions derived from imines and hydrazones undergo C-silylation in some cases. (a) Belavin, I. Yu.; Fedoseeva, N. A.; Baukov, Yu. I.; Lutsenko, I. F. *J. Gen. Chem. USSR (Engl. Transl.)* **1974**, *44*, 546–549. (b) Takabe, K.; Fujiwara, H.; Katagiri, T.; Tanaka, J. *Tetrahedron Lett.* **1975**, 1237–1238. (c) Corey, E. J.; Enders, D.; Bock, M. G. *Ibid.* **1976**, 7–10. (d) Corey, E. J.; Enders, D. *Chem. Ber.* **1978**, *111*, 1362–1383. (e) Fourtinnon, M.; de Jeso, B.; Pommier, J.-C. *J. Organomet. Chem.* **1980**, *193*, 165–174. See also: (f) Ahlbrecht, H.; Duber, E.-O. *Synthesis* **1980**, 630–631 and references cited therein.

(16) A representative hydrolysis procedure follows: To a solution of 10 mmol of imine 2 in 20 mL of CH₂Cl₂ was added 10 mL of 1 M acetic acid, and the mixture was stirred for 5 min at room temperature. The layers were separated, and the organic layer was diluted with ether and washed with aqueous NaHCO₃ and water, dried (MgSO₄), concentrated, and evaporatively distilled (oven temperature 55–60 °C, oil pump vacuum) to give the α -silyl aldehyde 3 as a low-melting solid, mp 44–50 °C. The hydrolysis of imine 4 was somewhat slower, requiring 30 min for completion.

(17) Oxidative cleavage of the corresponding dimethylhydrazones (Corey, E. J.; Enders, D. *Chem. Ber.* **1978**, *111*, 1337–1361; see also ref 15d) also led to predominant Si–C bond cleavage.

Scheme V^a

tions,¹⁸ the product β -hydroxy-*tert*-butyldimethylsilanes (**6**¹⁴ and **7**¹⁴) underwent smooth β elimination by using either the standard acidic ($\text{BF}_3\cdot\text{Et}_2\text{O}$) or basic (KH) conditions we have been using for β -hydroxytrimethylsilanes. Since the acid- and base-induced β -elimination reactions are known to be anti and syn respectively,⁵ the addition reactions to **5** must have taken place to form predominantly the *erythro*- β -hydroxysilane **7** (in accord with Cram's rule^{19,20}) in very high (up to 99%) stereoselectivity.

α -*tert*-Butyldimethylsilyl aldehydes can be used to introduce vinyl groups α to the carbonyl of both ketones and esters via reaction with the lithium enolates (Scheme III). The intermediate β -hydroxysilanes were frequently unstable to distillation and were generally purified only by placing under partial vacuum to remove volatile impurities. The β -elimination reactions were carried out with $\text{BF}_3\cdot\text{Et}_2\text{O}$; attempted β -elimination reactions with KH (of **10** and **14**) led to retro-aldol reactions. The preparation of *cis*- and *trans*-ketones **21** and **17** demonstrates that substituted vinyl (alkenyl) groups can be introduced α to carbonyl; the stereoselectivity is analogous to that observed in the reactions of **5** with organometallic reagents.²⁶

These reactions have also been used for the vinylation of an amino acid derivative. β,γ -Unsaturated amino acids have been of considerable recent interest because of their potent biological activity.²⁷ The stabase adduct **22**²⁸ of ethyl glycinate was con-

verted to the β -hydroxysilane **23**^{14a} in 93% yield (Scheme IV). Without purification, **23** was treated with $\text{BF}_3\cdot\text{Et}_2\text{O}$ in CH_2Cl_2 (room temperature, 16 h), effecting β elimination and deprotection of the amino group.²⁹ The aqueous extract was evaporated to dryness and hydrolyzed with 6 M HCl (reflux 3 h). Evaporation and cation exchange chromatography gave vinylglycine (**24**)³⁰ in 48% overall yield from **22**.

The use of **3** in a simple ring-growing sequence is shown in Scheme V in which KH effects both the β elimination and the anionic oxy-Cope rearrangement³¹ giving cyclodecenone³² in 49% overall yield from cyclohexanone. It should be noted that the final intermediate is an enolate anion which could, in principle, be used in another ring-growing sequence.

In summary, α -*tert*-butyldimethylsilyl aldehydes are readily prepared by hydrolysis of the corresponding imines and are versatile reagents for the stereoselective synthesis of α -vinyl-carbonyl compounds. Additionally, the intermediate β -hydroxysilanes in principle could serve as latent double bonds in synthetic schemes. We are examining further applications of these reactions.

Acknowledgment. We are grateful to Professor Carlyle B. Storm and Dr. Anne Turner for 200-MHz NMR spectra of compounds **17**, **19**–**21** and to Dr. Anne M. Hudrlik for useful discussions and assistance with the manuscript. We thank the National Science Foundation (Grants CHE 77-10523 and CHE 79-26181) and the Dow Corning Corporation for financial support.

(29) With shorter reaction times, only N-deprotection occurred.

(30) IR and NMR spectra of **24** were in excellent agreement with reported values (ref 27a,b); recrystallization from water-ethanol gave a sample with mp 215–218 °C dec (lit.^{27b} mp 218–220 °C dec).

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Pulsed Infrared Laser-Induced Reaction of Cyclobutyl Acetate. Laser Synthesis of a Thermally Labile Compound by a Rapid Heating–Quenching Process

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We report the laser synthesis of an organic compound which is thermally reactive when compared to its precursor, illustrating an unique application of pulsed infrared laser radiation that cannot be accomplished by conventional thermal techniques. During the past few years, many different types of compounds have been shown to undergo infrared multiphoton absorption to produce highly vibrationally excited ground electronic state molecules. The ability of the infrared laser to excite a molecule to high effective vibrational temperatures in $\sim 10^{-7}$ s has allowed unique transformations to be effected, including selective reaction of a single component in a mixture, control of chemical equilibria, reaction of a bifunctional reactant by the normally inaccessible higher energy pathway, and generation of high concentrations of transient intermediates.¹

The experimental methods are similar to those described elsewhere.^{2,3} Upon irradiation at 1078.6 cm^{-1} ($\text{R}(20)$ of 9- μm

(18) Some reactions which presumably involve nucleophilic attack at *t*- BuMe_2Si groups have shown to be about 10^4 times slower than those at Me_3Si groups: Åkerman, E. *Acta. Chem. Scand.* **1956**, *10*, 298–305; **1957**, *11*, 373–381.

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(20) Surprisingly high Cram's rule stereoselectivities have been previously observed in addition reactions of α -trimethylsilyl ketones^{8b,c,9b} and in the trapping of α -trimethylsilyl aldehydes (as presumed intermediates).^{11,12}

(21) The isomeric purities of olefins **8** and **9** were determined as in ref 11b.

(22) Ozeki, T.; Kusaka, M. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1995–1998.

(23) 2,4-DNP, mp 121–122 °C. Compound **13** was identical by IR and NMR spectra to a sample of **13** (2,4-DNP, mp 119.5–121 °C, satisfactory elemental analysis for C, H) prepared from the trimethylsilyl enol ether of pinacolone by addition of ethyl diazoacetate followed by reduction and treatment with acid (Hudrlik, P. F.; Bisaha, J. J., unpublished work; cf. ref 4).

(24) Crandall, J. K.; Arrington, J. P.; Hen, J. *J. Am. Chem. Soc.* **1967**, *89*, 6208–6213.

(25) With shorter reaction times, an intermediate believed to be a β -(trimethylsilyl)tetrahydrofuran was observed. On further treatment with $\text{BF}_3\cdot\text{Et}_2\text{O}$, this intermediate was converted to olefinic alcohol **19**.

(26) The stereochemistry of compounds **16**–**21** is based on 200-MHz NMR spectra of alcohols **19** and **20**, which showed olefinic proton coupling constants $J_{\text{trans}} = 15.3$ and $J_{\text{cis}} = 10.9$ Hz, respectively. Isomeric purities of olefinic ketones **17** and **21** were generally about 90–95% by VPC, depending on the particular batch of aldol **16** from which they were prepared.

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