fraction (f_t) of unconverted 1 at time t was determined from the IR spectra by using the ratio of the intensity of the absorption band at 5.7 μm, which is due to the carbonyl band for 1, to the intensity of the absorption band at 6.2 μm, which is an aromatic band found in all samples and, consequently, remains relatively constant. The decrease in f_t as a function of t is first order as shown in Figure 1, from which was deduced that the half-life of 1 under these conditions is about 90 h.

The NMR spectra of the samples, removed after 8, 76, and 296 h, showed that the components of the mixture were 1, 5, and 4 and that the corresponding ratio changed from 90:9:1 after 8 h to 6:3:1 after 76 h to 2:9:9 after 296 h.

(b) With NH_3 Vapor Saturated with H_2O To Give 4 (Expt 15). Experiment 14 was repeated with the modification that air was metered into the system after it was bubbled through concentrated aqueous NH_4OH (i.e., 30% NH_3). Samples were removed after 1.5, 3, 5, 6.5, and 22 h. The data (Figure 1) show that the conversion of 1 to products is first order and that the half-life for 1 under these conditions is about 2 h, which is considerably shorter than that with pure anhydrous NH_3 gas. The IR spectra of all but the last sample indicated that the product of interaction was the α form of 4. The IR spectrum of the last sample taken after 22 h showed that product mixture was mostly the β form of 4 (about 95%) with a small amount of the ammonium salt of *o*-acetamidobenzoic acid (about 5%).

(c) Reaction of 1 with Air Saturated with Water Vapor. The bottoms of two shallow weighing flasks were dusted evenly with a layer of finely powdered acetylanthranil. The flasks were then placed in a much larger closed chamber that was saturated with water vapor at 22 °C. One powdered sample was weighed periodically in order to monitor the increase in weight owing to reaction of 1 with H_2O to give *o*-acetamidobenzoic acid which occurs stoichiometrically. Small aliquots of powdered sample were removed periodically from the other flask to monitor by proton NMR in pyridine the conversion of acetylanthranil to *o*-acetamidobenzoic acid. The ratio of proton integrations for the methyl group of 1 to the sum total of proton integrations for the methyl groups in 1 and its product was used as a measure of mole fraction, x, of residual reactant at time t. This ratio was in good agreement with the corresponding ratio of the weight increase at time t to the total weight after 6 days in air saturated with water vapor at 22 °C. Both gave the same linear plot of log x as a function of t with a half-life $t_{1/2}$ = 35 h, as shown in Figure 1.

(3) Preparation of *o*-Acetamidobenzamide from *o*-Aminobenzamide. Powdered isatoic anhydride (30 g) was added to 100 cm^3 of a 10% aqueous ammonium hydroxide solution saturated with ammonium acetate. The mixture was warmed to initiate the reaction, which was accompanied by considerable frothing. When the frothing subsided, the mixture was heated on a steam bath with virgorous stirring for an additional hour. The clear solution was cooled to room temperature and *o*-amidobenzamide separated in the form of white platelets (21 g, mp 103–105 °C). The product was identified by its IR spectrum, which was identical with that of an authentic sample. The platelets were added to acetic anhydride (30 cm^3). Reaction occurred exothermically to give a clear solution, which crystallized on cooling to a dense mass of granular cubic crystals (21 g, mp 178–180 °C, with subsequent evolution of water at 235–270 °C to give 5 which solidified on cooling and remelted at 230-233 °C). This product was identified as the α form of *o*-acetamidobenzamide by its IR spectrum. After the α form was first isolated in our laboratory, however, subsequent attempts to prepare the α form via this procedure gave only the β form which melted at 186–188 °C.

The α and β forms and mixtures thereof could be recrystallized from MeOH and Me_2SO without change. Recrystallization from aqueous $NaHCO_3$, however, gives the β form exclusively. On the other hand, recrystallization of the β form from pyridine gives a mixture of the α and β forms, but the α form can be recovered unchanged from pyridine even after 3 days at reflux temperature.

(4) Conversion of 4 to 5 in Aqueous Solution at °C. A mixture of *o*-acetamidobenzamide (3.5 g, β form) and water (200 cm^3) was warmed to 90 °C in a three-necked, round-bottomed flask fitted with a stirrer, reflux condenser, and thermometer to give a clear solution, from which aliquot samples (10 cm^3) were removed periodically. Each sample was cooled to room temperature to induce crystallization. The precipitate was collected by filtration. The corresponding melting point and IR spectrum were noted to follow the conversion from 4 to 5 as a function of time. The fraction of 4 remaining unchanged at time t was calculated from the IR spectrum by using the absorption band at 13.3 μm, which is an aromatic band characteristic of the β form, as the indicator band and that at 6.3 μm, which is an aromatic band characteristic of both 4 and 5 and consequently remained essentially constant, as a reference band.

The fraction (f_t) of 4 not yet converted to 5 at time t is plotted in Figure 4 as a function of time. It shows that this conversion is first order and that the half-life of 4 under these reaction conditions is about 1 h. The corresponding melting point of the recovered solute at time t is also shown in Figure 4. It changed from 188–189 °C for pure 4 in its β form to a minimum of 163–168 °C at about 50% conversion to 5 and then up to 236–238 °C at 100% conversion to 5 showing that little or no side products are formed in the conversion.

Registry No. 1, 525-76-8; 2 (R = H), 7664-41-7; 4 (R = H), 33809-77-7; 5 (R = H), 1769-24-0; 7, 89-52-1; methyl *o*-acetamidobenzoate, 2719-08-6; *o*-aminobenzamide, 88-68-6.

Supplementary Material Available: The IR spectra and the X-ray diffraction patterns for the α and β forms of *o*-acetamidobenzamide (2 pages). Ordering information is given on any current masthead page.

Silanes in Organic Synthesis. 8. Preparation of Vinylsilanes from Ketones and Their Regiospecific Cyclopentenone Annulation[1]

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Received April 24, 1980

A general method is described for the formation of vinylsilanes from ketones. Thus, conversion to the benzene- or *p*-toluenesulfonylhydrazone and sequential treatment with *n*-butyllithium and chlorotrimethylsilane in anhydrous tetramethylethylenediamine proceeds regiospecifically to afford the less substituted vinylsilane (in unsymmetrical cases). Friedel–Crafts acylation with acryloyl chlorides and aluminum chloride and subsequent Nazarov cyclization with Lewis acid catalysis results in cyclopentenone annulation. Numerous examples that reveal the scope of this process are described. Due to accompanying polymerization, annulation with acryloyl chloride itself is least efficient. This complication can, however, be averted through use of β-chloropropionyl chloride and dehydrochlorination with 1,5-diazabicyclo[5.4.0]undec-5-ene prior to ring closure.

The decade of the 70's has witnessed the improvisation of a dazzling array of new methods for the construction of carbon–carbon bonds. Of these, the area commonly referred to as *vinylic substitution* has perhaps witnessed

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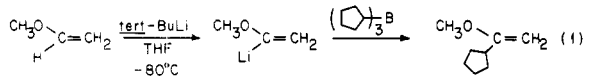
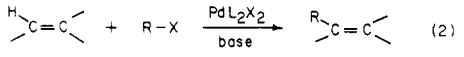
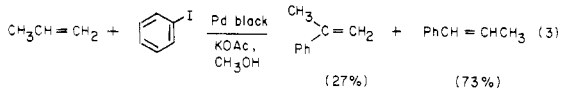
the greatest advances. As matters now stand, it is presently possible to *replace* an sp^2-bound hydrogen (or an appropriate equivalent) by means of carbanionic, transition-metal complex, and electrophilic chemistry. Where carbanion intermediates are concerned, heteroatom-assisted lithiations have gained considerable preparative importance.[4] In this instance, regiochemical control is dictated by the locus of the activating group (eq 1).[5]



Transition-metal catalysis has also fostered the development of this important field. In the presence of a catalytic amount of a palladium reagent, aryl, heterocyclic, benzylic, and vinyl bromides or iodides enter into efficient, stereospecific C–C bond making (eq 2).[6] The direction

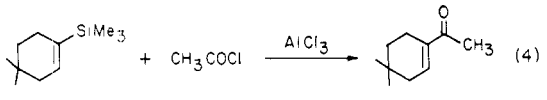


of addition of the organopalladium species to unsymmetrically substituted double bonds is largely sterically controlled, and, consequently, mixtures of products are usually formed (eq 3).[7] Added complications arise if more than



one sp^3-bonded hydrogen is situated β to the palladium group in the intermediate adduct.[6]

The orientation of electrophilic vinyl substitution is recognized to be controllable by the presence of a silicon substituent.[8] Due to the ease with which silicon can stabilize a β carbonium ion center, attack is directed to the carbon atom bonded to silicon (unless strong counterprevailing forces exist). Addition of the counterion does not usually follow;[9] rather, the silyl group undergoes facile displacement to regenerate the double bond (eq 4).[10]



The potential versatility of the latter method has suffered from the general unavailability of vinylsilanes. Certainly, a number of synthetic pathways to such compounds have been developed, particularly in the past several years; however, many are subject to substantive limitations. The most common restriction is that terminal vinylsilanes are most readily accessible. Methods in this category include 1,2-addition reactions of R_3SiCH_2MgX with aldehydes and ketones and subsequent dehydration, a variation of the Peterson olefination procedure in which the trisubstituted silyl group is not eliminated.[11] A closely related process is 1,2-addition of $[(CH_3)_3Si]_2CHLi$ to aldehydes and nonenolizable ketones with elimination of trimethylsilanoxide.[12] Lithium aluminum hydride reduction of $R_3SiC{\equiv}CCH_2OH$ is another method which requires a highly specific type of substrate.[13]

Procedures which result in the construction of internal vinylsilanes appear fraught with problems. Base-promoted cleavage reactions and eliminations lack the desired generality for true synthetic utility.[14] Hydrosilylation of acetylenes provides a route to vinylsilanes when symmetrical or terminal acetylenes are employed. Where unsymmetrical acetylenes are concerned, mixtures of vinylsilanes generally result, although the stereoselective production of a single isomer has been reported in certain specific circumstances.[15] Appropriate organometallics add across silylacetylenes to give substituted vinylsilanes. These reactions appear to be very sensitive to conditions and limited as to reactive substrate.[16-18] Hydroboration[9a,19] and hydroalumination[20] provide routes to internal vinylsilanes but again require a silylacetylene as starting material. Recently, two methods for the preparation of vinylsilanes of the type $R_3Si(R)C{=}CH_2$ have been developed starting from silylacetylenes[21] and 1-(trimethylsilyl)-1-bromoethene.[22] There also exists a selection of other schemes of little proven generality.[23]

Because the predescribed methods require a variety of starting materials which often are only indirectly available, universal adoption of any one of these schemes did not appear to us to hold promise. To bypass such complications and cause vinylsilanes to become readily available reagents for utilization in complex organic syntheses, we have developed a simple two-step procedure from ketonic precursors. The pivotal position of ketones and their ubiquitous nature require no comment. A preliminary description of this versatile synthetic method was reported by us in early 1977,[24] roughly concurrent with parallel

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(2) The Ohio State University Graduate (1975–1976) and Dissertation Fellow (1978–1979).

(3) Undergraduate research participant, 1976–1978.

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(9) A major exception to this general trend is bromination. For selected examples, see: (a) Miller, R. B.; Reichenbach, T. *Tetrahedron Lett.* **1974**, 543; (b) Jarvie, A. W. P.; Holt, A.; Thompson, J. *J. Chem. Soc. B* **1969**, 852; (c) Brook, A. G.; Duff, J. M.; Hitchcock, P.; Mason, R. *J. Organomet. Chem.* **1976**, *113*, C11; (d) Miller, R. B.; McGarvey, G. *J. Org. Chem.* **1978**, *43*, 4424; (e) Zweifel, G.; Lewis, W. *Ibid.* **1978**, *43*, 2739.

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(11) (a) Carey, F. A.; Toler, J. R. *J. Org. Chem.* **1976**, *41*, 1966 and relevant references cited therein. (b) Petrov, A. D.; Sadylch-Zade, J. I. *Dokl. Chem. (Engl. Transl.)* **1959**, *129*, 1033.

(12) (a) Grobel, B.-T.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 83; (b) Sachdev, K. *Tetrahedron Lett.* **1976**, 4041.

(13) Stork, G.; Jung, M. E.; Colvin, E.; Noel, Y. *J. Am. Chem. Soc.* **1974**, *96*, 3684. Silane additions to acetylenes are also well-recognized reactions.

(14) See for example: (a) Sommer, L. H., et al. *J. Am. Chem. Soc.* **1954**, *76*, 1613; (b) Sakurai, H.; Nishiwaki, K.; Kira, M. *Tetrahedron Lett.* **1973**, 4193.

(15) Consult: (a) Grerdtsiteli, I. M.; Baramidze, L. V. *J. Gen. Chem. USSR (Engl. Transl.)* **1968**, *38*, 1547; (b) Grerdtsiteli, I. M.; Baramidze, L. V. *Soobsch. Akad. Nauk Gruz. SSR* **1968**, *50*, 83; *Chem. Abstr.* **1968**, *69*, 77336.

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(17) Grignards: (a) Miller, R. B.; Reichenbach, T. *Synth. Commun.* **1976**, 319; (b) Snider, B. B.; Karras, M.; Conn, R. S. E. *J. Am. Chem. Soc.* **1978**, *100*, 4624.

(18) Nickel–aluminum complexes: (a) Snider, B. B.; Conn, R. S. E.; Karras, M. *Tetrahedron Lett.* **1979**, 1679; (b) Eisch, J. J.; Foxton, M. W. *J. Organomet. Chem.* **1968**, *12*, P33.

(19) Uchida, K.; Utimoto, K.; Nozaki, H. *J. Org. Chem.* **1976**, *41*, 2941.

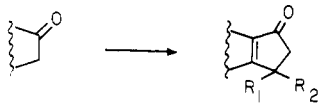
(20) (a) Uchida, K.; Utimoto, K.; Nozaki, N. *J. Org. Chem.* **1976**, *41*, 2215. (b) Eisch, J. J.; Damasevitz, G. A. *Ibid.* **1976**, *41*, 2214.

(21) Hudrlik, P. F.; Schwartz, R. H.; Hogen, J. C. *J. Org. Chem.* **1979**, *44*, 155.

(22) Huynh, C.; Linstrumelle, G. *Tetrahedron Lett.* **1979**, 1073.

(23) (a) Larsson, E.; Knopp, L.-O. *Acta Chem. Scand.* **1947**, *1*, 268. (b) Märkl, G.; Hofmeister, P. *Tetrahedron Lett.* **1976**, 3419. (c) Jaffe, C. *J. Organomet. Chem.* **1970**, *23*, 53.

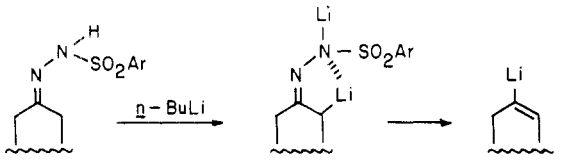
studies conducted independently by the research groups of Chan[25] and Bond.[26] Herein, we shall direct discussion to the details of this transformation in a large number of examples. A vinylsilane-mediated cyclopentenone annulation sequence of general scope which allows for the transformation illustrated by eq 5[27a] is also fully described.[27b]



(5)

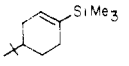
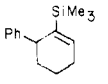
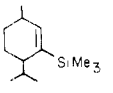
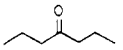
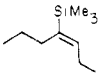
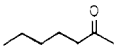
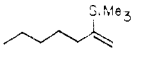
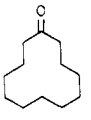
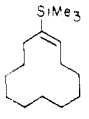
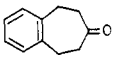
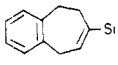
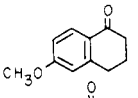
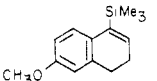
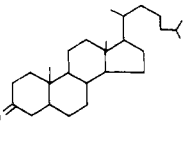
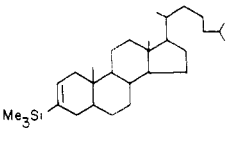
Preparation of the Vinylsilanes. A requisite feature of the new strategem was that it allow for the formation of internal vinylsilanes having well-defined regiochemistry and double bond stereochemistry. Furthermore, the method was necessarily to make use of a readily available functional group, preferably with utilization of well-developed chemistry so as to allow for sound predictability of product structure. To these ends, the present approach takes advantage of the proclivity of arenesulfonylhydrazones for conversion to vinyl carbanion intermediates with greater than 2 equiv of *n*-butyllithium in *N,N,N',N'*-tetramethylethylenediamene (TMEDA) solution[28] and the ready in situ reaction of these anions with commercially available chlorotrimethylsilane. Importantly, the trimethylsilyl group becomes bonded exclusively to the original carbonyl carbon.

The conversion of arenesulfonylhydrazones to vinyl carbanions is a well-studied process, protonation of the intermediate carbanion with resultant olefin formation being referred to as the Shapiro reaction.[29] The direction of deprotonation of the arenesulfonylhydrazone is recognized to be highly controlled.[28,29] As with dimethylhydrazones[30] and oximes,[31,32] it is the proton positioned syn to the arenesulfonylhydrazone which is abstracted (eq 6).[33] This kinetic bias appears to be directed by chelation



(6)

Table I. Summary of Ketone Enesilylations[47]

ketone	arenesulfonyl hydrazone (% yield)[a]	vinylsilane	yield, %
	BSH (81)		50
	BSH (92)		87
	BSH (93)		94
	TSH (80)		97
	BSH (69)		91
	BSH (74)		48
	BSH (b)		85
	BSH (91)		97
	TSH (75)		84
	BSH (94)		b
	BSH (93)		95
	BSH (83)		88
	BSH (76)		67
	BSH (67)		67
	BSH (85)		b
	BSH (b)		50

[a] BSH = benzenesulfonylhydrazone; TSH = *p*-toluenesulfonylhydrazone. [b] Yield not determined.

of the alkyllithium base to the hydrazone nitrogen. Therefore, it follows that vinyl carbanion production is subject to the same regiochemical restraints, since conversion to the vinyllithium species proceeds by a nonrandomization mechanism.[29,33]

In general, steric factors largely control arenesulfonylhydrazone stereochemistry, the bulky $NHSO_2Ar$ group

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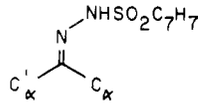
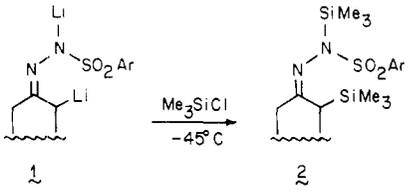
(26) Chamberlin, A. R.; Stemke, J. E.; Bond, F. T. *J. Org. Chem.* **1978**, *43*, 147.
(27) (a) Fristad, W. E.; Dime, D. S.; Bailey, T. R.; Paquette, L. A. *Tetrahedron Lett.* **1979**, 1999. (b) Cooke, F.; Moerck, R.; Schwindeman, J.; Magnus, P. *J. Org. Chem.* **1980**, *45*, 1046.
(28) (a) Stemke, J. E.; Bond, F. T. *Tetrahedron Lett.* **1975**, 1815. (b) Stemke, J. E.; Chamberlin, A. R.; Bond, F. T. *Ibid.* **1976**, 2947. (c) Traas, P. C.; Boelens, H.; Takken. H. J. *Ibid.* **1976**, 2287.
(29) (a) Shapiro, R. H.; Heath, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 5734. (b) Kaufman, G.; Cook, F.; Shechter, H.; Bayless, J.; Friedman, L. *Ibid.* **1967**, *89*, 5736. (c) Shapiro, R. H. *Org. React.* **1976**, *23*, 405.
(30) (a) Corey, E. J.; Enders, D. *Tetrahedron Lett.* **1976**, 3, 11. (b) Corey, E. J.; Enders, D.; Buck, M. G. *Ibid.* **1976**, 7. (c) Corey, E. J.; Knapp, S. *Ibid.* **1976**, 4687.
(31) (a) Spencer, T. A.; Leong, C. W. *Tetrahedron Lett.* **1975**, 3889. (b) Kofron, W. G.; Yeh, M. K. *J. Org. Chem.* **1976**, *41*, 439. (c) Jung, M. E.; Blair, P. A.; Lowe, G. A. *Tetrahedron Lett.* **1976**, 1439. (d) Lyle, R. E.; Saevedra, J. E.; Lyle, G. G.; Fribush, H. M.; Marshal, J. L.; Lijinski, W.; Singer, G. M. *Ibid.* **1976**, 4431. (e) Fraser, R. R.; Dhawan, K. L. *J. Chem. Soc., Chem. Commun.* **1976**, 674. (f) Park, C. A.; Beam, C. F.; Kaiser, E. M.; Kaufman, R. F.; Heroch, F. E.; Hansen, C. R. *J. Heterocycl. Chem.* **1976**, *13*, 449. (g) Geam, C. F., et al. *Ibid.* **1976**, *13*, 607. (h) Jung, M. E.; Shaw, T. J.; Fraser, R. R.; Banville, J.; Taymaz, K. *Tetrahedron Lett.* **1979**, 4149.
(32) For additional pertinent references, consult: (a) Jung, M. E.; Shaw, T. T. *Tetrahedron Lett.* **1977**, 3305; (b) Ensley, H. E.; Lohr, R. *Ibid.* **1978**, 1415. (c) Bergbreiter, D. E.; Newcomb, M. *Ibid.* **1979**, 4145. This last paper should be consulted with regard to the question of deprotonation regioselectivity.
(33) (a) Shapiro, R. H.; Lipton, M. F.; Kolonko, K. J.; Buswell, R. L.; Capuano, L. A. *Tetrahedron Lett.* **1975**, 1811. (b) Dauben, W. G.; Rivers, G. T.; Zimmerman, W. T.; Yang, N. C.; Kim, B.; Yang, J. *Ibid.* **1976**, 2951. (c) Lipton, M. F.; Shapiro, R. H. *J. Org. Chem.* **1978**, *43*, 1409.

positioning itself syn to the less substituted side of the original carbonyl. For this reason, the vinyllithium produced is always the less substituted one. An additional restraint is that the newly developed double bond must be of *Z* geometry if unfavorable interactions between the substituent on the incipient olefin and $NHSO_2Ar$ are to be minimized.[34] In substrates which are closely balanced sterically, it now appears possible to establish tosylhydrazone stereochemistry by determination of the ^{13}C NMR chemical shifts of the α-methylene carbons.[35] Due to steric compression, $\delta(C_\alpha) < \delta(C'_\alpha)$. In comparisons of their ^{13}C shifts with those of the derived ketones, C_α was seen to differ by 12–15 ppm, whereas C'_α showed $\Delta\delta$'s of 3–6 ppm.



At the experimental level, examination of numerous sets of reaction conditions has led us ultimately to a procedure which efficiently, frequently in excess of 90%, delivers vinylsilanes contaminated by the corresponding olefin. More specifically, the arenesulfonylhydrazone (Table I) is added at −45 °C to a solution of excess *n*-butyllithium in TMEDA. Under these conditions, a dianion such as **1** is formed. The stability of this species at this temperature was proven by the addition of chlorotrimethylsilane and isolation of a ditrimethylsilylated species of type **2**.



When the mixture was warmed to above −30 °C, dianion **1** spontaneously decomposed to the vinyl carbanion, nitrogen, and arenesulfinate anion. This process can be easily followed by observing the formation of nitrogen bubbles. The resulting monolithium species is then trapped with chlorotrimethylsilane to generate the desired vinylsilane.

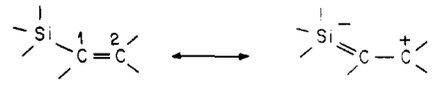
Stringently anhydrous conditions are necessary to avoid concomitant formation of the corresponding olefin. This necessitates the use of TMEDA (which can be recycled for subsequent reuse) as solvent, since ethereal solvents are slowly deprotonated by the highly basic vinyl carbanion. The amine solvent also retards decomposition of the arenesulfinate anion to sulfur dioxide and arene anion. This side reaction has previously been observed to cause complications when tetrahydrofuran was utilized as solvent.[26] Likewise, the hydrolytically unstable chlorotrimethylsilane must be *freshly distilled from calcium hydride*, as even newly opened bottles contained quantities of hydrogen chloride adequate to cause production of relatively large quantities of olefin. Transfers of this reagent were always accomplished by syringe techniques.

According to the proposed mechanism, only 2 equiv of base are required to generate a vinyl carbanion. We have observed, however, that at least 3 equiv of base are needed to maximize the yield of vinylsilane. This is the result of additional partial deprotonation of the arenesulfinate anion. As shown by Bond,[26] the consumption of excess base can be precluded by the use of 2,4,6-triisopropylbenzenesulfonylhydrazones. Excess *n*-butyllithium was simply used throughout this study.

As with most synthetic methods, the present sequence suffers from certain limitations. The most obvious of these is the requirement for substrate stability to alkyllithium reagents. Second, aldehyde arenesulfonylhydrazones do not undergo the reaction. Such compounds have been shown to experience 1,2-addition across the carbon–nitrogen double bond with eventual decomposition to a secondary alkyllithium.[36] The lack of deprotonation on carbon can be satisfactorily explained in terms of the absence of a chelation effect, the hydrazone moiety expectedly being positioned syn to the aldehyde hydrogen. Finally, the control of temperature must be more closely monitored when certain phenyl or benzyl ketones are used in order to preclude partial conversion to the allyl anion.[1b]

Despite these drawbacks, the sequence has much to commend it. The conditions are extremely mild, it being possible to conduct the various steps of the reaction below 0 °C. The ready availability of precursors and reagents, the overall simplicity of the reaction conditions, and the amenability to acid-sensitive functionality are some factors which should foster future recourse to vinylsilane production in this manner.

Spectral Properties of Vinylsilanes. To our knowledge, the ^1H and ^{13}C NMR spectra of vinylsilanes have been discussed only briefly in the literature.[37,38] Nevertheless, a trend is quite obvious. As a result of the weak d_π–p_π electron-withdrawing capability of the trimethylsilyl substituent, vinylsilanes possess an intrinsic mesomeric nature which positively polarizes the β carbon atom (eq 7). As a result, protons attached to C_2 and the



(7)

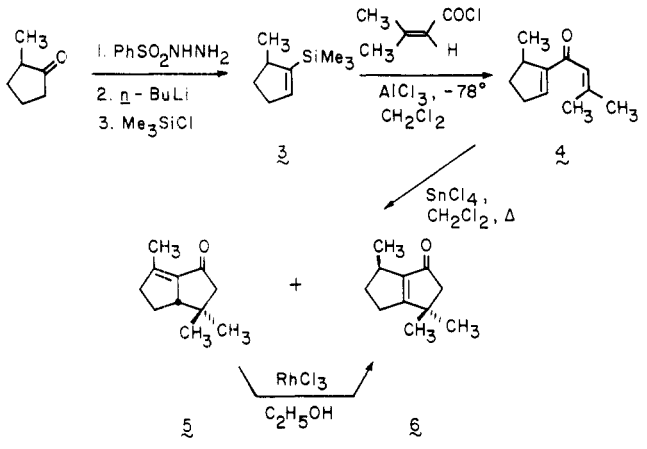
carbon atoms themselves are deshielded relative to C_1. Typically, the β proton appears in the vicinity of δ 6.0 if this position is monoalkyl substituted; in the case of a terminal vinyl group, the multiplet is centered in the vicinity of δ 5.5. These data are to be contrasted with the chemical shifts of enamines where a reversal in polarization results in shielding at the β site.[39]

The nature of bonding in vinylsilanes has also been investigated by mass and photoelectron spectroscopy.[40]

Regiospecific Cyclopentenone Annulation of Ketones. The efficient conversion of a ketone to a fused cyclopentenone as in eq 5 constitutes an important annulation process. Not only does a new five-membered ring result, but the endocyclic, carbon–carbon double bond provides for subsequent control of ring-fusion stereochemistry, stereoselective attachment of appendages and/or functional groups, and ring expansion through cleavage when the starting material is cyclic. Although various methods have been utilized to achieve this end result ($R_1 = R_2 = H$[41] and $R_1 = R_2 = CH_3$[42]), the availa-

(34) Kolonko, K. J.; Shapiro, R. H. *J. Org. Chem.* **1978**, *43*, 1404 and relevant references cited therein.
(35) Bunnell, C. A.; Fuchs, P. L. *J. Org. Chem.* **1977**, *42*, 2614.
(36) Vedejs, E.; Stolle, W. T. *Tetrahedron Lett.* **1977**, 135.
(37) (a) Hengge, E.; Pletka, H. D. *Monatsh. Chem.* **1973**, *104*, 1365. (b) Rakita, P. E.; Worsham, L. S. *J. Organomet. Chem.* **1977**, *139*, 135.
(38) Chan, T. H.; Mychajlowskij, W.; Amouroux, R. *Tetrahedron Lett.* **1977**, 1605.
(39) Stork, G.; Brizzolara, A.; Landesman, H.; Szmuszkovicz, J.; Terrell, R. *J. Am. Chem. Soc.* **1963**, *85*, 207.
(40) (a) Bock, H.; Seidl, H. J. *J. Organomet. Chem.* **1968**, *13*, 87. (b) Weidner, U.; Schweig, A. *Ibid.* **1972**, *39*, 261.

Scheme I

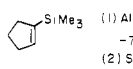
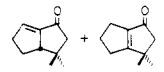
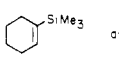
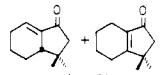
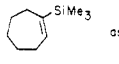
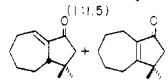
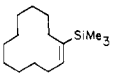
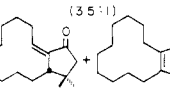
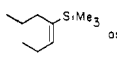
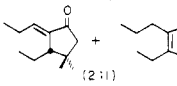
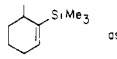
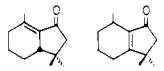


bility of a general procedure remains highly desirable.

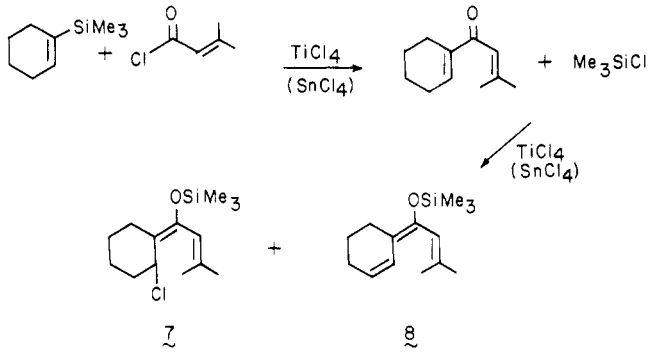
Annulation processes mediated through a carbonyl group may suffer from lack of regiospecificity when the second bond of the pendant five-membered ring is formed.[41e,43] Often the locus of annulation is dependent upon the course of the dehydration of an alcohol resulting from nucleophilic attack on the carbonyl.[41b-d,44] In some cases, prior activation of an α position by a carbomethoxy group,[45] an enamine,[46a-c] or a silyl enol ether[46d] is necessary to ensure regiospecificity. The method herein described utilizes the almost universal regiospecificity of ketone enesilylation[47] to ensure proper orientation of the annulated cyclopentenone. The trimethylsilyl group is recognized to powerfully activate and direct the Friedel–Crafts acylation of a vinylsilane,[8a] resulting in the acylium ion becoming bonded directly to the silicon-bearing carbon with subsequent loss of the trimethylsilyl group.[8,10,48]

Pentadienyl cations are well-known to undergo conrotatory electrocyclic ring closure.[49] These cations have been generated from a number of species, including conjugated enyne alcohols,[50] acetylenic diols,[41b,c,42a,44a] α,β-unsaturated esters,[51] α'-(trimethylsiloxy)-α,β-unsaturated ketones,[44b] hydroxydichloro olefins,[44a] and, most importantly, dienones.[52] All of the above examples have involved generation

Table II. Cyclopentenone Annulation of Vinylsilanes with β,β-Dimethylacryloyl Chloride

vinylsilane	reacn condtn	initial cyclization products	yield, %	Rh(III) catalysis product	overall yield, %
	(1) $AlCl_3$, CH_2Cl_2 −78°, 15 min (2) $SnCl_4$, CH_2Cl_2, reflux 8–12 hrs	 (1:1.5)	–		62
	as above	 (1:1.5)	–		70
	as above	 (3.5:1)	57		
	(1) as above (2) $BF_3 \cdot Et_2O$, C_6H_6, reflux 1–3 days	 (3:2)	43		
	as above	 (2:1)	62		
	as above	 (1:1)	–		60

Scheme II



of the pentadienyl cation under protic acid conditions. No previous study of dienone cyclizations under catalysis by Lewis acids has been uncovered. In our hands, this modification has much to recommend it (vide infra).

The overall concept is illustrated for the specific case of 2-methylcyclopentanone in Scheme I. Reaction of **3** with 1 equiv each of β,β-dimethylacryloyl chloride and aluminum chloride in anhydrous dichloromethane at −78 °C for 5 min effected conversion to **4** which was isolated but not purified. Treatment of **4** with 3 equiv of stannic chloride in refluxing dichloromethane for 3 days followed by preparative layer chromatography produced a mixture of **5** and **6** in isolated yields of 33 and 19%, respectively. Alternatively, exposure of the enone mixture to rhodium(III) chloride trihydrate in hot ethanol[53] prior to purification gave rise exclusively to **6** (55%). The structural assignment to **6** follows from its lithium in liquid ammonia reduction to *exo-cis*-4,4,8-trimethylbicyclo[3.3.0]octan-2-one, which was independently synthesized by lithium dimethylcuprate addition to *exo-cis*-4,8-dimethylbicyclo[3.3.0]oct-3-en-2-one.[54]

(41) (a) Paquette, L. A.; Wyvratt, M. J.; Schallner, O.; Schneider, D.; Begley, W. J.; Blankenship, R. M. *J. Am. Chem. Soc.* **1976**, *98*, 6744; *J. Org. Chem.* **1979**, *44*, 3616. (b) MacAlpine, G. A.; Raphael, R. A.; Shaw, A.; Taylor, A. W.; Wild, H.-J. *J. Chem. Soc., Chem. Commun.* **1974**, 834. (c) Karpf, M.; Dreiding, A. S. *Helv. Chim. Acta* **1976**, *59*, 1226. (d) Hiyama, T.; Shinoda, M.; Nozaki, H. *Tetrahedron Lett.* **1978**, 771. (e) Trost, B. M.; Keeley, D. E. *J. Am. Chem. Soc.* **1976**, *98*, 250. See also earlier references cited in these papers.

(42) (a) Baumann, M.; Hoffmann, W.; Müller, N. *Tetrahedron Lett.* **1976**, 3585. (b) Cooke, F.; Schwindeman, J.; Magnus, P. *Ibid.* **1979**, 1995. (c) See also: Altenbach, H.-J. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 940.

(43) Trost, B. M.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 289.

(44) (a) Hiyama, T.; Shinoda, M.; Nozaki, H. *J. Am. Chem. Soc.* **1979**, *101*, 1599. (b) Jacobson, R. M.; Lahn, G. L. *J. Org. Chem.* **1979**, *44*, 462.

(45) (a) Marino, J. P.; Landrick, R. C. *Tetrahedron Lett.* **1975**, 4531. (b) Dauben, W. G.; Hart, D. *J. Org. Chem.* **1977**, *42*, 922.

(46) (a) Hayakawa, Y.; Yokoyama, K.; Noyori, R. *J. Am. Chem. Soc.* **1978**, *100*, 1799. (b) Jacobson, R. M.; Rath, R. A.; MacDonald, J. H., III. *J. Org. Chem.* **1977**, *42*, 2545. (c) Corey, E. J.; Boger, D. T. *Tetrahedron Lett.* **1978**, 13. (d) Miyashita, M.; Yanami, T.; Yoshikashi, A. *J. Am. Chem. Soc.* **1976**, *98*, 4679.

(47) The term enesilylation refers to the conversion of a ketone to a vinylsilane where the C–Si bond has replaced the original carbonyl group.

(48) (a) Dey, K.; Eaborn, C.; Walton, D. R. M. *Organomet. Chem. Synth.* **1971**, 151. (b) Chan, T. H. *Acc. Chem. Res.* **1977**, *10*, 442.

(49) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim/Bergstr., Germany, **1971**.

(50) Vartanyan, S. A.; Chukhadzhyan, G. A. *Izv. Akad. Nauk Arm. SSR, Khim. Nauki* **1959**, *12*, 179; *Chem. Abstr.* **1960**, *54*, 7707e.

(51) Conia, J.-M.; Leriverend, M.-L. *Bull. Soc. Chim. Fr.* **1970**, 2981.

(52) (a) Nazarov, I. N.; Zaretskaya, I. I. *J. Gen. Chem. USSR (Engl. Transl.)* **1959**, *29*, 1532. (b) Braude, E. A.; Coles, J. A. *J. Chem. Soc.* **1950**, 2014; **1952**, 1430. (c) Luhowry, R.; Keehn, P. M. *Tetrahedron Lett.* **1976**, 1043. (d) Shoppee, C. W.; Cooke, B. J. A. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2271; **1973**, 1026. (e) Dev, S. *J. Indian Chem. Soc.* **1957**, *34*, 169.

(53) (a) Grieco, P. A.; Hishizawa, M.; Marinovic, N. *J. Am. Chem. Soc.* **1976**, *98*, 7102. (b) Andrieaux, J.; Barton, D. H. R.; Patin, H. *J. Chem. Soc., Perkin Trans. 1* **1977**, 359.

During the development of reaction conditions suitable for ring closure, several key factors were identified. These include the order in which the various reagents are introduced, the particular Lewis acid employed, the temperature, and the workup procedure.

The order of mixing of the reagents proved particularly crucial in obtaining high yields. Addition of the Lewis acid directly to a solution containing only vinylsilane resulted in partial conversion to olefin. This event, of course, eliminates the possibility of control of acylation regiochemistry. Furthermore, *olefins are generally insufficiently reactive to experience acylation under the mild conditions applicable to vinylsilanes.*[55] Addition of the Lewis acid to a solution of acid chloride followed by the vinylsilane proved to be the more efficacious procedure.

Reaction at the lowest convenient temperature resulted in fewest side reactions. At −78 °C, acylation with β,β-dimethylacryloyl chloride was frequently complete within 5 min (Table II); however, little or no cyclization ensued under these conditions. At 0 °C, cyclization did occur, but large amounts of undesirable silyl enol ether formation and 1,4-addition of chloride ion were also seen (see below).

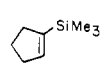
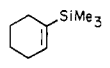
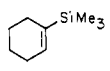
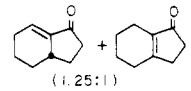
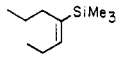
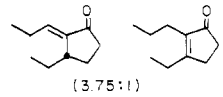
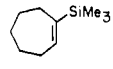
The choice of Lewis acid still remains a hit or miss situation. In several instances, a catalyst observed to work well with certain substrates proved pernicious with another. Titanium tetrachloride, a routinely poor choice, gave mixtures of up to six products from simple acylation efforts. Dominant pathways are illustrated in Scheme II. On the other hand, boron trifluoride etherate at low temperatures (−78 to 0 °C) neither promoted acylation of the vinylsilane nor formed a colored complex. Stannic chloride led to facile acylation of the vinylsilane but also gave partial 1,4-addition of chlorotrimethylsilane (see **7**). The tendency of these Lewis acids to catalyze 1,4-addition may be the result of crowded coordination spheres which prohibit them from tightly binding to all of the chloride ligands. The small ionic radius of titanium(IV), 0.68 Å, makes it a more serious offender than tin(IV), 0.71 Å. For the minimization of the 1,4-addition problem, aluminum chloride was investigated as catalyst. Tetrachloroaluminate anion appears to remain more tightly coordinated, as it gives rise to little or no 1,4-addition, while promoting essentially instantaneous acylation of vinylsilanes. This is not to say that $AlCl_3$ does not induce silyl enol ether formation (e.g., **8**); however, such an intermediate is converted to the desired dienone on hydrolytic workup. For this very reason, a two-step procedure must be employed for the annulation, as the intermediate silyl enol ethers expectedly resist cyclization and do not interconvert with the dienone under the requisite anhydrous conditions.

The optimum conditions for annulation with β,β-dimethylacryloyl chloride involved acylation with aluminum chloride catalysis followed by stirring of the product with dilute hydrochloric acid to liberate the dienone. This acid treatment did not reverse the 1,4-addition of chlorotrimethylsilane (as in **7**) when it occurred but delivered a β-chloro enone. At this point, the dienone could be cyclized in a second step by treatment with a several-fold excess of a Lewis acid. Stannic chloride proved to be the most useful catalyst for this purpose; however, in some cases boron trifluoride etherate was used advantageously (Table II).

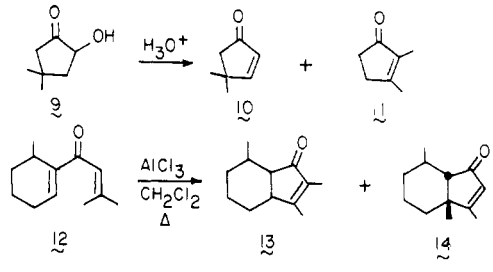
In certain circumstances, care must be exercised not to induce rearrangement either during the cyclization or after

(54) Achmad, S. A.; Cavill, G. W. K. *Aust. J. Chem.* **1965**, *18*, 1989.
(55) Schostarez, H. J., unpublished findings.

Table III. Cyclopentenone Annulation of Vinylsilanes with Crotonyl and Acryloyl Chlorides

vinylsilane	reacn condtn	cyclization product	yield, %
A. Crotonyl Chloride			
	(1) $AlCl_3$, CH_2Cl_2, −78°, 15 min. (2) $BF_3 \cdot Et_2O$, C_6H_6, reflux 3 days		58
	(1) $AlCl_3$, CH_2Cl_2, R.T., 1 hr (2) $BF_3 \cdot Et_2O$, C_6H_6, reflux		44
B. Acryloyl Chloride			
	$AlCl_3$, CH_2Cl_2, R.T., 2 hr.	 (1.25:1)	27
	as above	 (3.75:1)	24
	(1) $AlCl_3$, NaOAc, CH_2Cl_2, −45°, 15 min. (2) CF_3COOH, R.T., 3 hr.		10

formation of the cyclopentenone. Precedent for such complications is seen in earlier reports which describe the dehydration of **9** in aqueous acid as leading to mixtures



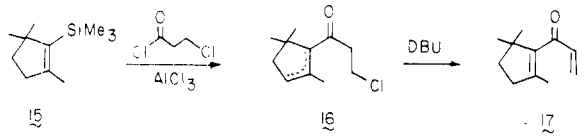
of **10** and **11**.[56] Indeed, when the cyclization of **12** was carried out with aluminum chloride, only products of rearrangement were observed. Cyclization with stannic chloride, on the other hand, produced no undesired rearranged cyclopentenones.

The cyclized products were often obtained as mixtures of double bond isomers. Although the endocyclic/exocyclic ratios expectedly vary from system to system, this phenomenon has presented no complications because of the efficiency and thermodynamic control associated with Rh(III)-promoted isomerization of these mixtures.

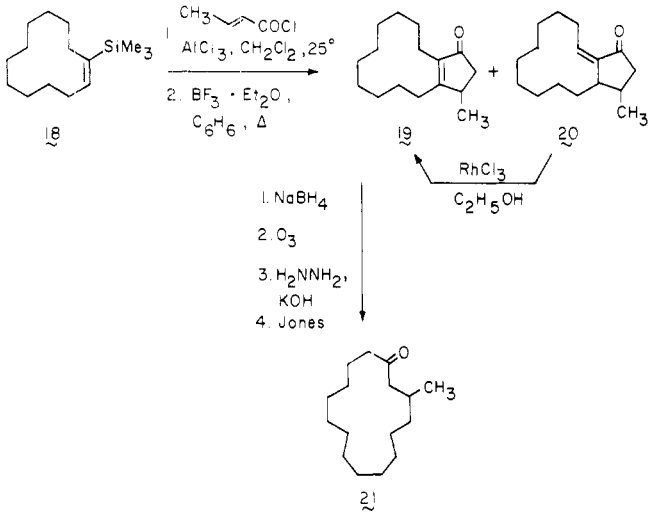
A comparison of the data contained in Tables II and III reveals that respectable yields are realized with β,β-dimethylacryloyl and crotonyl chlorides, while acryloyl chloride lacks practical utility. These results appear to arise from a combination of factors, the major being the ease and cleanness of the acylation. In this regard, the relative rate of acylation was noted to decrease with a lessening of the degree of methyl substitution on the acid halide. Whereas condensation with β,β-dimethylacryloyl chloride was complete within several minutes at −78 °C, crotonyl chloride occasionally required 1 h at room temperature to proceed to completion. Reactions with acryloyl chloride were less predictable due to simultaneous de-

(56) (a) Agosta, W. C.; Smith, A. B., III. *J. Am. Chem. Soc.* **1971**, *93*, 5513. (b) Bellamy, A. J. *J. Chem. Soc. B* **1969**, 449. (c) Compare: Crouse, R. S. *J. Org. Chem.* **1961**, *26*, 3525.

Scheme III



Scheme IV



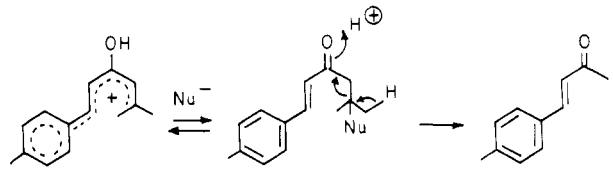
struction of products. Thus, there exists a correlation between the order of acylium ion stability and ease of vinylsilane acylation.

The problems associated with acryloyl chloride can be nicely circumvented by substitution of commercially available β-chloropropionyl chloride. As exemplified in Scheme III, the vinylsilane acylation step can be conducted without risk of polymerization. Ultimate treatment of the mixture of enones **16** with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) gave the isomerically homogeneous dienone **17**. This alternative would appear to have broad synthetic potential.

Cleavage of the cyclopentenone double bond for overall ring expansion of a cyclic ketone is typified by the formal conversion of 1-(trimethylsilyl)cyclododecene (**18**) to (±)-muscone (**21**) (Scheme IV).[57] Upon condensation of **18** with crotonyl chloride in the presence of $AlCl_3$, the resulting dienone was cyclized with boron trifluoride etherate in hot benzene to give a mixture of **19** and **20** in 48 and 18% isolated yields. Since **20** could be quantitatively isomerized to **19** under conditions of Rh(III) catalysis, this separation becomes unnecessary. Sequential ozonolysis of the derived carbinol, Wolff–Kishner reduction, and oxidation has been shown by Baumann and co-workers[42a] to deliver **21**.

Finally, we point out certain idiosynchrosies of the Nazarov reaction. With the intent of preparing β-cuparenone (**27**),[58] our target became cyclopentenone **26** since it had previously been shown that **26** can serve as a precursor to **27**.[58g] The requisite vinylsilane, because it is formally derived by enesilylation[47] of an aldehyde, had to be prepared indirectly. This was achieved by bromodecarboxylation of *p*-methylcinnamic acid (**22**), low-temperature halogen–metal exchange, and chlorotrimethylsilane quenching (Scheme V). During the production of **24**, a small amount of *p*-tolylacetylene was formed by base-promoted elimination of hydrogen bromide. The separation of this impurity was achieved chromatographically. Treatment of **24** with β,β-dimethylacryloyl chloride and aluminum chloride in dichloromethane at −78 °C afforded dienone **25** quantitatively. Assignment of the *E* olefin geometry is based on the observed coupling constant (16 Hz) between the styrene protons and the anticipated desilylation from the less hindered rotamer.

Dienone **25** proved highly resistant to cyclization. With stannic chloride, **25** was recovered intact. Boron trifluoride etherate produced a separable mixture of recovered **25** (31%), the desired **26** (10%), and decomposition products. Despite many efforts, this set of conditions turned out to be uniquely effective. Harsher Lewis acid conditions led solely to decomposition. With trifluoroacetic acid, no reaction occurred at room temperature, and total decomposition was seen at 70 °C. When dienone **25** was refluxed in ethanolic hydrochloric acid, a procedure developed by Shoppee for other phenyl-substituted dienone systems,[52d] *p*-methylbenzylidene acetone (**29**) was formed cleanly.



Concentrated sulfuric acid in glyme solution produced an analogous result, whereas the less nucleophilic FSO_3H in chloroform had no effect other than protonation of the system. Evidently, cation **28** is too stable to overcome the necessary activation energy for irreversible cyclization to the complexed or protonated cyclopentenone.

Experimental Section

Proton magnetic resonance spectra were recorded with Varian A-60A, EM-360, and T-60 spectrometers as well as a Bruker HX-90 spectrometer. Apparent splittings are given in all cases. Infrared spectra were recorded on a Perkin-Elmer Model 467 instrument. Mass spectra were determined on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Preparation of the Arenesulfonylhydrazones. The ketone (1 equiv) was dissolved in absolute ethanol along with the benzene- or *p*-toluenesulfonylhydrazide (1 equiv) and a catalytic amount of *p*-toluenesulfonic acid. The mixture was heated to reflux under nitrogen for 0.4–5 h and cooled. The crystals so obtained were filtered and recrystallized from ether–hexane. If crystals did not precipitate from solution, the reaction mixture was concentrated, and the oily residue was taken up in ether and precipitated by the addition of hexane.

Cyclopentanone benzenesulfonylhydrazone: 81%; mp 151–156 °C; ^1H NMR ($CDCl_3$) δ 8.0–7.8 (m, 2 H), 7.6–7.4 (m, 3 H), 2.5–2.1 (m, 4 H), 2.0–1.7 (m, 4 H).

Cyclohexanone benzenesulfonylhydrazone: 92%; mp 145–150 °C (lit.[25] mp 143–145 °C); ^1H NMR ($CDCl_3$) δ 8.0–7.8 (m, 2 H), 7.5–7.3 (m, 3 H), 2.4–2.0 (m, 4 H), 1.7–1.5 (m, 6 H).

Cycloheptanone benzenesulfonylhydrazone: 93%; mp 146–147 °C (lit.[25] mp 146–148 °C); ^1H NMR ($CDCl_3$) δ 8.0–7.8

(57) For previous *dl*-muscone syntheses, see footnote 1 in: Stork, G; McDonald, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 1264. More recent additions to this list include ref 42a and: Taguchi, H.; Yamamoto, H.; Nozaki, H. *Tetrahedron Lett.* **1976**, 2617; Fischli, A.; Branca, Q.; Daly, J. *Helv. Chim. Acta* **1976**, *59*, 2443; Ito, Y.; Saegusa, T. *J. Org. Chem.* **1977**, *42*, 2326.

(58) For previous syntheses, consult: (a) Parker, W.; Ramage, R.; Raphael, R. A. *J. Chem. Soc.* **1962**, 558; (b) Lansbury, P. T.; Hilfiker, F. R. *J. Chem. Soc. D* **1969**, 619; (c) Lansbury, P. T.; Nienhouse, E. J.; Scharf, D. J.; Hilfiker, F. R. *J. Am. Chem. Soc.* **1970**, *92*, 5649; (d) Mane, R. B.; Rao, G. S. K. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1706; (e) Leverend, P. *Bull. Soc. Chim. Fr.* **1973**, 3498; (f) DeMayo, P.; Swan, R. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2559; (g) Casares, A.; Maldonado, L. A. *Synth. Commun.* **1976**, *6*, 11.

(m, 2 H), 7.5–7.3 (m, 3 H), 2.5–2.2 (m, 4 H), 1.9–1.4 (m, 8 H).

4-*tert*-Butylcyclohexanone tosylhydrazone: 80%; mp 148–150 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.75 (d, J = 8 Hz, 2 H), 7.22 (d, J = 8 Hz, 2 H), 2.42 (s, 3 H), 2.2–1.0 (m, 9 H), 0.90 (s, 9 H).

2-Methylcyclohexanone benzenesulfonylhydrazone: 69%; ^{1}H NMR ($CDCl_3$) δ 8.0–7.8 (m, 2 H), 7.6–7.3 (m, 3 H), 2.5–1.4 (br m, 9 H), 1.0 (d, J = 6 Hz, 3 H).

2-Phenylcyclohexanone benzenesulfonylhydrazone: 74%; mp 119–121 °C; ^{1}H NMR ($CDCl_3$) δ 7.8–7.0 (br m, 5 H), 3.5 (t, J = 6 Hz, 1 H), 2.5–1.8 (br m, 8 H).

***dl*-Menthone benzenesulfonylhydrazone**: mp 131–133 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.0–7.8 (m, 2 H), 7.6–7.3 (m, 4 H), 2.7–2.4 (m, 1 H), 2.0–1.3 (m, 7 H), 0.98 (d, J = 5 Hz, 3 H), 0.90 (d, J = 6 Hz, 3 H), 0.50 (d, J = 6 Hz, 3 H).

4-Heptanone benzenesulfonylhydrazone: 91%; mp 102–104 °C (lit.[25] mp 102–103 °C); ^{1}H NMR ($CDCl_3$) δ 8.0–7.8 (m, 2 H), 7.6–7.4 (m, 3 H), 2.4–1.9 (m, 4 H), 1.8–1.2 (m, 4 H), 0.83 (q, J = 7 Hz, 6 H).

2-Heptanone tosylhydrazone: 75%; mp 82–83 °C; ^{1}H NMR ($CDCl_3$) δ 7.57 (d, J = 8 Hz, 2 H), 7.20 (d, J = 8 Hz, 3 H), 2.40 (s, 3 H), 2.2–2.0 (m, 2 H), 1.76 (s, 3 H), 1.6–0.8 (m, 9 H).

Propiophenone benzenesulfonylhydrazone: 94%, mp 137–139 °C; ^{1}H NMR ($CDCl_3$) δ 8.1–7.9 (m, 2 H), 7.5–7.2 (m, 8 H), 2.66 (q, J = 7 Hz, 2 H), 1.17 (t, J = 7 Hz, 3 H).

Cyclododecanone benzenesulfonylhydrazone: 93%; mp 163–168 °C; ^{1}H NMR ($CDCl_3$) δ 8.0–7.8 (m, 2 H), 7.6–7.4 (m, 3 H), 2.2 (br t, J = 6 Hz, 4 H), 2.0–1.8 (br m, 20 H).

4,5-Benzocycloheptenone benzenesulfonylhydrazone: 83%; mp 159 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.8 (m, 2 H), 7.4 (m, 2 H), 7.05 (s, 4 H), 3.0–2.4 (br m, 8 H).

α-Tetralone benzenesulfonylhydrazone: 76%; mp 191–192 °C dec (lit.[25] mp 185–187 °C); ^{1}H NMR ($CDCl_3$) δ 8.2–7.8 (m, 4 H), 7.6–7.4 (m, 3 H), 7.2–7.0 (m, 3 H), 2.9–2.3 (m, 4 H), 2.2–1.8 (m, 2 H).

6-Methoxy-α-tetralone benzenesulfonylhydrazone: 67%; mp 198–200 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.0–7.8 (m, 3 H), 7.5–7.3 (m, 3 H), 6.70 (m, 1 H), 6.58 (m, 1 H), 4.70 (s, 3 H), 2.8–2.4 (m, 4 H), 2.0–1.7 (m, 2 H).

2,2-Dimethylcyclohexanone benzenesulfonylhydrazone: 85%; mp 164 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.0–7.8 (m, 2 H), 7.6–7.2 (m, 4 H), 2.4–2.1 (m, 2 H), 1.8–1.4 (m, 6 H), 1.07 (s, 6 H).

Cholestanone Benzenesulfonylhydrazone. Cholestanone (5.0 g, 12.9 mmol) and benzenesulfonylhydrazide (2.58 g, 15 mmol) were dissolved in warm absolute ethanol (230 mL), and concentrated hydrochloric acid (2.5 mL) was added to make a 0.4% hydrochloric acid–ethanol solution. The reaction mixture was heated at reflux under an argon atmosphere for 30 min, cooled, and evaporated. The concentrated residue was diluted with benzene and heated on a steam bath to azeotropically remove residual water and ethanol. The product was recrystallized from benzene–hexane to furnish powdery white crystals, mp 213 °C dec.

Preparation of the Vinylsilanes. A dry, three-necked flask equipped with a stirring bar, a nitrogen inlet, a rubber septum, and an Erlenmeyer flask containing the arenesulfonylhydrazone (ca. 5 g) connected by a short piece of Gooch tubing was charged with dry TMEDA. The solvent was cooled to −45 °C, and n-butyllithium (4 equiv) in hexane was introduced via syringe. To this cold solution was slowly added in portions the arenesulfonylhydrazone. A dark red color developed immediately. Upon completion of the addition (10–20 min), the solution was stirred for an additional 30–60 min before it was allowed to warm to room temperature for 1–2 h. During this time, nitrogen was evolved. When nitrogen evolution had ceased, the red solution was cooled to 0 °C, and chlorotrimethylsilane (4 equiv) was slowly injected from a syringe. The solution generally lightened to a yellow color and then slowly turned black. After being stirred at 0 °C for 30 min, the reaction mixture was allowed to warm to room temperature where it was kept for several hours prior to being poured into water (200 mL) and pentane (100 mL). The organic layer was separated and subsequently extracted with water (2 × 200 mL), saturated copper sulfate solution (2 × 200 mL), and brine (100 mL). The dried solution was concentrated, applied to neutral alumina, and eluted with pentane through a short (5 cm) plug of neutral alumina to remove the colored material. The eluant was concentrated and used as obtained or was distilled. Varying amounts of octane as an impurity from n-butyllithium coupling were present in the unpurified vinylsilane samples.

1-(Trimethylsilyl)cyclopentene: 50%; bp 106–108 °C; ^{1}H NMR ($CDCl_3$) δ 6.00 (m, 1 H), 2.7–2.2 (m, 4 H), 2.2–1.6 (m, 2 H), 0.21 (s, 9 H). Anal. Calcd for $C_8H_{16}Si$: C, 68.46; H, 11.52. Found: C, 68.34; H, 11.60.

1-(Trimethylsilyl)cyclohexene: 87%; bp 70–78 °C (33 torr); ^{1}H NMR (C_6D_6) δ 6.12 (m, 1 H), 2.12 (m, 4 H), 1.72 (m, 4 H), 0.22 (s, 9 H). Anal. Calcd for $C_9H_{18}Si$: C, 70.04; H, 11.75. Found: C, 70.15; H, 11.84.

1-(Trimethylsilyl)cycloheptene: 94%; bp 94–95 °C (20 torr); ^{1}H NMR ($CDCl_3$) δ 6.23 (m, 1 H), 2.5–2.1 (m, 4 H), 2.1–1.3 (m, 6 H), 0.18 (s, 9 H). Anal. Calcd for $C_{10}H_{20}Si$: C, 71.34; H, 11.98. Found: C, 71.35; H, 11.91.

1-(Trimethylsilyl)-4-*tert*-butylcyclohexene: 97%; bp 55–59 °C (0.3 torr); ^{1}H NMR ($CDCl_3$) δ 6.14 (m, 1 H), 2.46–1.06 (m, 7 H), 0.99 (s, 9 H), 0.24 (s, 9 H). Anal. Calcd for $C_{13}H_{26}Si$: C, 74.20; H, 12.46. Found: C, 74.18; H, 12.43.

2-(Trimethylsilyl)-3-methylcyclohexene: 91%; bp 95–105 °C (28 torr); ^{1}H NMR ($CDCl_3$) δ 5.98 (m, 1 H), 2.6–1.6 (br m, 7 H), 1.05 (d, J = 7 Hz, 3 H), 0.14 (s, 9 H). Anal. Calcd for $C_{10}H_{20}Si$: C, 71.38; H, 11.97. Found: C, 71.42; H, 11.86.

2-(Trimethylsilyl)-3-phenylcyclohexene: 48%; ^{1}H NMR ($CDCl_3$) δ 7.2 (s, 5 H), 6.16 (br t, J = 3 Hz, 1 H), 3.5 (m, 1 H), 2.3–2.0 (m, 2 H), 2.0–1.5 (m, 4 H), 0.10 (s, 9 H); mass spectrum, m/e calcd 230.1491, obsd 230.1497.

2-(Trimethylsilyl)-3-isopropyl-6-methylcyclohexene: 85%; bp 95–111 °C (7 torr); ^{1}H NMR ($CDCl_3$) δ 5.93 (m, 1 H), 2.2–1.4 (br m, 7 H), 0.97 (d, J = 7 Hz, 6 H), 0.73 (d, J = 7 Hz, 3 H), 0.03 (s, 9 H).

(*E*)-4-(Trimethylsilyl)-3-heptene: 97%; bp 43 °C (32 torr); ^{1}H NMR ($CDCl_3$) δ 5.76 (t, J = 7 Hz, 1 H), 2.4–1.9 (m, 4 H), 1.74–1.24 (m, 2 H), 1.2–0.7 (m, 6 H), 0.15 (s, 9 H). Anal. Calcd for $C_{10}H_{22}Si$: C, 70.49; H, 13.02. Found: C, 70.64; H, 13.03.

2-(Trimethylsilyl)-1-heptene: 84%; bp 79–83 °C (27 torr); ^{1}H NMR ($CDCl_3$) δ 5.57 (m, 2 H), 2.2–0.9 (m, 11 H), 0.13 (s, 9 H).[12a]

(*E*)-1-(Trimethylsilyl)-1-phenylpropene: ^{1}H NMR ($CDCl_3$) δ 7.3–6.8 (m, 5 H), 6.16 (q, J = 7 Hz, 1 H), 1.90 (d, J = 7 Hz, 3 H), 0.12 (s, 9 H). Anal. Calcd for $C_{12}H_{18}Si$: C, 75.72; H, 9.53. Found: C, 75.71; H, 9.62.

(*E*)-1-(Trimethylsilyl)cyclododecene: 95%; bp 115–120 °C (3 torr); ^{1}H NMR ($CDCl_3$) δ 5.80 (br t, J = 8 Hz, 1 H), 2.5–2.0 (m, 4 H), 1.6–1.3 (m, 16 H), 0.10 (s, 9 H); mass spectrum, m/e calcd 238.2117, obsd 238.2121.

1-(Trimethylsilyl)-4,5-benzo-1,4-cycloheptadiene: 88%; ^{1}H NMR ($CDCl_3$) δ 7.4–7.1 (m, 4 H), 6.05 (br t, J = 6 Hz, 1 H), 3.8–3.5 (m, 2 H), 3.3–3.0 (m, 2 H), 2.7–2.4 (m, 4 H), 0.10 (s, 9 H); mass spectrum, m/e calcd 216.1334, obsd 216.1338. Anal. Calcd for $C_{14}H_{20}Si$: C, 77.70; H, 9.32. Found: C, 77.99; H, 9.33.

1-(Trimethylsilyl)-3,4-dihydronaphthalene: 67%; bp 65–80 °C (0.1 torr); ^{1}H NMR ($CDCl_3$) δ 7.3–7.1 (m, 4 H), 6.50 (t, J = 4 Hz, 1 H); 3.0–2.7 (m, 2 H), 2.6–2.2 (m, 2 H), 0.40 (s, 9 H).

1-(Trimethylsilyl)-3,4-dihydro-6-methoxynaphthalene: 67%; bp 95 °C (0.1 torr); ^{1}H NMR ($CDCl_3$) δ 7.15 (m, 1 H), 6.8–6.6 (m, 2 H), 6.34 (t, J = 4 Hz, 1 H), 3.83 (s, 3 H), 3.0–2.6 (m, 2 H), 2.5–2.1 (m, 2 H), 0.35 (s, 9 H).

2-(Trimethylsilyl)-3,3-dimethylcyclohexene: bp 70–75 °C (4 torr); ^{1}H NMR ($CDCl_3$) δ 6.87 (t, J = 3 Hz, 1 H), 2.1–1.1 (series of m, 6 H), 0.92 (s, 6 H), 0.00 (s, 9 H); mass spectrum, m/e calcd 182.1491, obsd 182.1495.

3-(Trimethylsilyl)-2-cholestene: 50%; mp 158–165 °C (from methanol); ^{1}H NMR ($CDCl_3$) δ 6.0–5.5 (m, 1 H), 2.1–0.7 (series of m, 46 H), 0.1 (s, 9 H); mass spectrum m/e calcd 442.3995, obsd 442.4004.

General Procedure for Annulation with β,β-Dimethylacryloyl Chloride. In a dry, two-necked flask equipped with a nitrogen inlet and rubber septum were placed dry dichloromethane (8 mL) and anhydrous aluminum chloride (1.0 mmol). The slurry was cooled to −78 °C, and β,β-dimethylacryloyl chloride (1.0 mmol) was added via syringe followed by the vinylsilane (1.0 mmol). The solution turned slightly yellow during 30 min before being poured into 3 M hydrochloric acid (10 mL). After being stirred vigorously for 15 min, the reaction mixture was diluted with ether, and the layers were separated. The organic phase was extracted with water (10 mL), a saturated solution of sodium

bicarbonate (10 mL), and brine (10 mL). The solution was dried and evaporated, and the residue was dissolved in dry dichloromethane (10 mL) and transferred to a round-bottomed flask. To this solution was added stannic chloride (3.0 mmol), and the solution was heated to reflux. The progress of reaction was monitored by thin-layer chromatography and was allowed to proceed until the starting dienone was completely consumed. The purple-red solution was poured onto 1.5 M hydrochloric acid and diluted with ether. The organic layer was extracted with water (10 mL), a saturated solution of sodium bicarbonate (10 mL), and brine (10 mL) before being dried. The concentrated residue was chromatographed (silica gel, elution with 50% ether/hexane) to yield the cyclized product. Final purification was accomplished by preparative VPC (see Table II for yields).

A. From 1-(Trimethylsilyl)cyclopentene. 3,3-Dimethyl-3a,4,5-trihydro-2*H*-pentalen-1-one: bp 44–46 °C (0.3 torr); ^{1}H NMR ($CDCl_3$) δ 6.40 (m, 1 H), 3.3–2.5 (m, 2 H), 2.34 (br d, 2 H), 2.1–1.5 (m, 2 H), 1.13 (s, 3 H), 0.82 (s, 3 H); ν_{max} (film) 3000, 1715, 1640, 1220 cm^{-1}; mass spectrum, m/e calcd 150.1045, obsd 150.1048. **3,3-Dimethyl-4,5,6-trihydro-2*H*-pentalen-1-one:** bp 44–46 °C (0.3 torr); ^{1}H NMR ($CDCl_3$) δ 2.53 (s, 2 H), 2.32 (br s, 6 H), 1.20 (s, 6 H); ν_{max} (film) 2940, 1700, 1640, 1370, 1275, 1030 cm^{-1}; mass spectrum m/e calcd 150.1045, obsd 150.1048.

B. From 1-(Trimethylsilyl)cyclohexene. 3,3-Dimethyl-3a,4,5,6-tetrahydro-2*H*-indan-1-one: 2,4-dinitrophenylhydrazone, mp 182–183 °C; ^{1}H NMR ($CDCl_3$) δ 6.68 (br, d, J = 3 Hz, 1 H), 2.4–1.3 (m, 6 H), 2.10 (s, 2 H), 1.17 (s, 3 H), 0.78 (s, 3 H); ν_{max} (film) 2940, 2860, 1720, 1655, 1220 cm^{-1}; mass spectrum, m/e calcd 164.1201, obsd 164.1205. **3,3-Dimethyl-4,5,6,7-tetrahydro-2*H*-indan-1-one:** 2,4-dinitrophenylhydrazone, mp 242–243 °C (lit.[51] mp 242.5–243.5 °C); ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 2 H), 2.2–1.9 (m, 4 H), 1.8–1.4 (m, 4 H), 1.14 (s, 6 H); ν_{max} (film) 2900, 1690, 1645, 1410, 1380, 1245 cm^{-1}; mass spectrum, m/e calcd 164.1201, obsd 164.1205.

C. From 1-(Trimethylsilyl)cycloheptene. 3,3-Dimethyl-3a,4,5,6,7-pentahydro-2*H*-azulen-1-one: bp 65–68 °C (0.1 torr); ^{1}H NMR ($CDCl_3$) δ 6.9 (m, 1 H), 2.6–1.4 (m, 9 H), 2.22 (s, 2 H), 1.25 (s, 3 H), 0.90 (s, 3 H); ν_{max} (film) 2930, 2860, 1720, 1645, 1240 cm^{-1}; mass spectrum, m/e calcd 178.1358, obsd 178.1362. Anal. Calcd for $C_{12}H_{18}O$: C, 80.55; H, 10.53. Found: C, 80.77; H, 10.44. **3,3-Dimethyl-4,5,6,7,8-pentahydro-2H-azulen-1-one:** bp 65–68 °C (0.1 torr); ^{1}H NMR ($CDCl_3$) δ 2.6–1.4 (m, 8 H), 2.3 (s, 2 H), 1.23 (s, 6 H); ν_{max} (film) 2920, 2850, 1695; 1640, 1440, 1285 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.53. Found: C, 80.64; H, 10.22.

D. From 1-(Trimethylsilyl)cyclododecane. 15,15-Dimethylbicyclo[10.3.0]pentadec-11-en-13-one: ^{1}H NMR ($CDCl_3$) δ 6.53 (dd, J = 10, 4 Hz, 1 H), 2.7–1.0 (m, 21 H), 1.05 (s, 3 H), 0.80 (s, 3 H). **15,15-Dimethylbicyclo[10.3.0]pentadec-12-en-13-one:** ^{1}H NMR ($CDCl_3$) δ 2.5–2.0 (m, 4 H), 2.23 (s, 2 H), 2.0–1.3 (m, 14 H), 1.24 (s, 6 H); ν_{max} (film) 2980, 1700, 1625, 1470, 1440, 1355 cm^{-1}. Anal. Calcd for $C_{17}H_{28}O$: C, 82.18; H, 11.38. Found: C, 82.05; H, 11.36.

E. From (*E*)-4-(Trimethylsilyl)-3-heptene. 2-Propylidene-3-ethyl-4,4-dimethylcyclopentanone: ^{1}H NMR ($CDCl_3$) δ 6.5 (dt, J = 7, 2 Hz, 1 H), 2.5–0.8 (m, 13 H), 1.20 (s, 3 H), 1.00 (s, 3 H); mass spectrum, m/e calcd 180.1514, obsd 180.1519. **2-Propyl-3-ethyl-4,4-dimethylcyclopentenone:** ^{1}H NMR ($CDCl_3$) δ 2.6–1.9 (m, 6 H), 1.6–1.2 (m, 2 H), 1.2–0.8 (m, 6 H), 1.10 (s, 6 H); mass spectrum, m/e calcd 180.1514, obsd 180.1519. Anal. Calcd for $C_{12}H_{20}O$: C, 79.95; H, 11.17. Found: C, 79.73; H, 11.19.

F. From 2-(Trimethylsilyl)-3-methylcyclohexene. 3,3,7-Trimethyl-3a,4,5,6-tetrahydro-2*H*-indan-1-one: ^{1}H NMR ($CDCl_3$) δ 2.05 (s, 3 H), 2.3–0.9 (br m, 9 H), 1.10 (s, 3 H), 0.75 (s, 3 H); ν_{max} (film) 2930, 1710, 1640, 1450, 1220 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O$: C, 80.82; H, 10.21. Found: C, 80.66; H, 10.19. **3,3,7-Trimethyl-4,5,6,7-tetrahydro-2*H*-indan-1-one:** ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 2 H), 2.5–1.2 (m, 7 H), 1.10 (s, 6 H), 1.08 (d, J = 8 Hz, 3 H); ν_{max} (film) 2960, 1695, 1640, 1460, 1245 cm^{-1}; mass spectrum, m/e calcd 178.1358, obsd 178.1362. Anal. Calcd for $C_{12}H_{18}O$: C, 80.82; H, 10.21. Found: C, 80.41; H, 10.43.

3,3,6-Trimethyl-3a,4,5-trihydro-2*H*-pentalen-1-one (5) and 3,3,6-Trimethyl-4,5,6-trihydro-2*H*-pentalen-1-one (6). Treatment of 2-methylcyclopentanone benzenesulfonylhydrazone (26.4 g, 0.112 mol) with *n*-butyllithium (350 mL of 1.6 M solution in hexane, 0.56 mol) in anhydrous TMEDA (350 mL) in the predescribed manner (1 h at −45 °C, 5 h at 45 °C) followed by chlorotrimethylsilane (71 mL, 0.56 mol) at 0 °C (and overnight at room temperature) gave 10.90 g (64%) of 2-(trimethylsilyl)-3-methylcyclopentene (**3**): bp 75–85 °C (60 torr); ^{1}H NMR ($CDCl_3$) δ 5.8 (m, 1 H), 2.4–1.8 (m, 2 H), 1.3–0.7 (m, 3 H), 0.93 (d, J = 6.5 Hz, 3 H), 0.05 (s, 9 H). Anal. Calcd for $C_9H_{18}Si$: C, 70.04; H, 11.75. Found: C, 70.07; H, 11.83.

Acylation of **3** (200 mg, 1.29 mmol) with β,β-dimethylacryloyl chloride (152 mg, 1.29 mmol) in dichloromethane (15 mL) containing 170 mg (1.29 mmol) of anhydrous aluminum chloride in the usual manner and subsequent cyclization of the hydrolyzed reaction mixture in dry dichloromethane (15 mL) containing stannic chloride (3.75 mmol) (reflux under nitrogen for 3 days) furnished 71.7 mg (33%) of **5** and 40 mg (19%) of **6**. Separation was achieved by preparative VPC (6 ft × 0.25 in. column, 5% SE-30, 148 °C); both isomers were isolated as clear colorless oils.

For **5**: ^{1}H NMR ($CDCl_3$) δ 3.4–0.8 (series of m, 7 H), 2.02 (m, 3 H), 1.15 (s, 3 H), 0.86 (s, 3 H); ν_{max} (film) 1703, 1656, 1627 cm^{-1}; mass spectrum, m/e calcd 164.1201, obsd 164.1204.

For **6**: ^{1}H NMR ($CDCl_3$) δ 3.2–0.8 (series of m, 7 H), 1.21 (s, 3 H), 12.0 (s, 3 H), 1.12 (d, J = 6.5 Hz, 3 H); ν_{max} (film) 1697, 1638 cm^{-1}; mass spectrum, m/e calcd 164.1201, obsd 164.1205. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.31; H, 9.85.

Rhodium Chloride Promoted Isomerization of 5. A mixture of **5** (15.2 mg) and **6** (25.9 mg) was made up, and 24.8 mg of this sample was treated with 3 mg of rhodium trichloride hydrate in 1 mL of deoxygenated absolute ethanol at reflux temperature under nitrogen for 2 days. The cooled reaction mixture was poured onto water (50 mL) and extracted with dichloromethane (3 × 15 mL). The combined organic layers were washed with water (50 mL), dried, and concentrated to give 24.5 mg of pure **6**.

Dissolving-Metal Reduction of 6. To a 100-mL, three-necked flask fitted with a dry ice condenser, an argon gas inlet tube, a magnetic stirring bar, and a rubber septum was added 30 mL of dry liquid ammonia followed by an 80-mg piece of lithium wire (ca. 10 equiv). A solution of **6** (185 mg, 1.13 mmol) in ether (5 mL) containing water (20 mg) was added, and the solution was stirred at −78 °C for 1 h under argon. Solid ammonium chloride was added to discharge the blue color, and the ammonia was allowed to evaporate. The residue was taken up in dichloromethane (50 mL) and water (50 mL). After the mixture was shaken, the layers were separated, and the aqueous phase was again extracted with dichloromethane (3 × 15 mL). The combined organic layers were washed with water (30 mL), dried, and concentrated to leave a yellow oil which was taken up in 5 mL of acetone.

Jones reagent was added dropwise to this solution until the red color persisted. Follwing the addition of enough isopropyl alcohol to discharge the color, the reaction mixture was processed by dichloromethane extraction of the product from water. The resultant yellow oil (161 mg) consisted of three components which were separated on the 5% SE-30 column at 139 °C.

The most rapidly eluted compound (35%) proved to be identical with *exo-cis*-4,4,8-trimethylbicyclo[3.3.0]octan-2-one as prepared by the following procedure. The second component was the endo cis isomer (50%): ^{1}H NMR ($CDCl_3$) δ 3.0–0.8 (series of m, 9 H), 1.16 (s, 3 H), 1.03 (s, 3 H), 1.01 (d, J = 7 Hz, 3 H); ν_{max} (film) 1735 cm^{-1}; mass spectrum m/e calcd 166.1358, obsd 166.1361. The third component (15%) was unreduced starting material.

***exo-cis*-4,4,8-Trimethylbicyclo[3.3.0]octan-2-one.** Into a 100-mL, three-necked flask equipped with a magnetic stirring bar, rubber septum, and nitrogen inlet was weighed 919 mg (4.5 mmol) of cuprous iodide. The flask was flame-dried, and, after the flask cooled, 45 mL of anhydrous ether was added, and the mixture was cooled to 0 °C. Methyllithium (6 mL of a 1.75 M solution in ether, 9.14 mmol) was introduced via syringe under nitrogen, the mixture was stirred for 5 min, and *exo-cis*-4,8-dimethylbicyclo[3.3.0]oct-3-en-2-one[54] (595 mg, 3.97 mmol) was added dropwise from a syringe. After being stirred at 0 °C for 2.5 h, the reaction mixture was poured into dilute hydrochloric acid (100 mL) and filtered through Celite. The filter cake was washed with pentane (100 mL), and the pentane and aqueous layers were shaken and separated. The water layer was extracted further with pentane (3 × 50 mL), and the combined hydrocarbon solutions

were washed with water (200 mL), dried, and concentrated. There was obtained 603 mg (93%) of the title ketone; ^{1}H NMR ($CDCl_3$) δ 2.45–0.8 (series of m, 9 H), 1.14 (s, 3 H), 1.13 (d, J = 6 Hz, 3 H), 1.07 (s, 3 H); ν_{max} (film) 1739 cm^{-1}; mass spectrum, m/e 166.1358, obsd 166.1361; $[\alpha]^{23}_D$ +189°. Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.62; H, 10.93.

Isomerization of 3,3-Dimethyl-3a,4,5-trihydro-2*H*-pentalen-1-one to 3,3-Dimethyl-4,5,6-trihydro-2*H*-pentalen-1-one. The mixture of internal and external enones (50 mg, 0.33 mmol) was dissolved in ethanol/water (10/1, 1.1 mL) and deoxygenated by bubbling nitrogen through the solution for 5 min. Rhodium(III) chloride trihydrate (5 mg, 0.02 mmol) was added, and the solution was refluxed under nitrogen for 16 h. The black solution was cooled, diluted with ether, washed with water, and dried. The concentrated residue was chromatographed (silica gel, elution with 50% ether/hexane) to give only the internal enone (50 mg, 100%).

Isomerization of 3,3,7-Trimethyl-3a,4,5,6-tetrahydro-2*H*-indan-1-one and 3,3,7-Trimethyl-4,5,6,7-tetrahydro-2*H*-indan-1-one. By use of the above procedure, an equilibrium mixture of the internal and external enones was obtained after refluxing for 25 h. After chromatography, the title enones were obtained in 11 and 71% yields, respectively.

Annulations with Crotonyl Chloride. A. From 1-(Trimethylsilyl)cyclopentane. By use of the general procedure outlined earlier (see also Table III), 3-methyl-4,5,6-trihydro-2*H*-pentalen-1-one was isolated in 58% yield: ^{1}H NMR ($CDCl_3$) δ 3.3–0.85 (series of m, 9 H), 1.21 (d, J = 7 Hz, 3 H); ν_{max} (film) 1694, 1640 cm^{-1}; mass spectrum, m/e calcd 136.0889, obsd 136.0891; 2,4-dinitrophenylhydrazone, mp 214.5–215 °C (lit.[59] mp 214.5–215 °C).

B. From 1-(Trimethylsilyl)cyclohexene. 3-Methyl-4,5,6,7-tetrahydro-2*H*-indan-1-one: ^{1}H NMR ($CDCl_3$) δ 3.0–0.85 (series of m, 11 H), 1.18 (d, J = 8 Hz, 3 H); ν_{max} (film) 1700 cm^{-1}; mass spectrum, m/e calcd 150.1045, obsd 150.1047; 2,4-dinitrophenylhydrazone, mp 242.5–243.5 °C (lit.[51,59] mp 242.5–243.5 °C).

C. From 1-(Trimethylsilyl)cyclododecene. 15-Methylbicyclo[10.3.0]pentadec-12-en-13-one (19): mp 53–54 °C; ^{1}H NMR ($CDCl_3$) δ 3.1–0.9 (series of m, 23 H), 1.14 (d, J = 7.5 Hz, 3 H); ν_{max} (film) 1699, 1640 cm^{-1}; mass spectrum m/e calcd 234.1984, obsd 234.1990. Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.85; H, 11.00. **15-Methylbicyclo[10.3.0]-pentadec-11-en-13-one (20):** ^{1}H NMR ($CDCl_3$) δ 6.6–6.4 (br dd, 1 H), 3.0–0.8 (series of m, 22 H), 0.96 (d, J = 7 Hz, 3 H); ν_{max} (film) 1717, 1643 cm^{-1}; mass spectrum, m/e calcd 234.1984, obsd 234.1992.

Isomerization of 20 to 19. A mixture of **19** (19.8 mg) and **20** (12.7 mg) in 1 mL of deoxygenated ethanol was heated at reflux with 3 mg of $RhCl_3 \cdot H_2O$ under nitrogen for 2 days. The customary workup afforded 32 mg of pure **19**.

Annulations with Acryloyl Chloride. A. 3,3a,4,5,6-Pentahydro-2*H*-indan-1-one and 3,4,5,6,7-Pentahydro-2*H*-indan-1-one. Aluminum chloride (402 mg, 3.0 mmol) was slurried in dry dichloromethane (10 mL) and cooled to −20 °C. To the cooled slurry was added acryloyl chloride (90 mg, 1.0 mmol) followed by 1-(trimethylsilyl)cyclohexene (170 mg, 1.0 mmol). The stirred mixture was warmed to room temperature and poured, after 2 h, onto 2 M hydrochloric acid, and the mixture was vigorously stirred for 30 min. The organic layer, which was diluted with ether and separated, was washed with a saturated solution of sodium bicarbonate (10 mL), dried, and evaporated. The residue was chromatographed (silica gel, elution with 50% ether/hexane) to yield the external enone [20 mg (15%); ^{1}H NMR ($CDCl_3$) δ 6.45 (m, 1 H), 2.5–1.0 (m, 11 H); ν_{max} (film) 2900, 1715, 1650, 1220 cm^{-1}] and the internal enone [17 mg (12%); ^{1}H NMR ($CDCl_3$) δ 2.5–1.9 (m, 8 H), 1.8–1.5 (m, 4 H); ν_{max} (film) 2910, 1690, 1645, 1390 cm^{-1}].

B. 2-Propylidene-3-ethylcyclopentanone and 2-Propyl-3-ethylcyclopent-2-enone. Aluminum chloride (161 mg, 1.2 mmol) was slurried in dry dichloromethane (5 mL) and cooled to −20 °C. Acryloyl chloride (108 mg, 1.2 mmol) and 4-(trimethylsilyl)hept-3-ene (202 mg, 1.19 mmol) were then added, and the mixture was stirred in the cold for 15 min. The solution was stirred with 3 M hydrochloric acid, diluted with ether, and separated. The organic phase was washed with water, a saturated solution of sodium bicarbonate, and brine, prior to drying and solvent removal. The residue was dissolved in trifluoroacetic acid (2 mL) and stirred at room temperature under nitrogen for 3 h. The solution was slowly added to a saturated solution of sodium bicarbonate, and the organic material was extracted into dichloromethane. The organic layer was dried and evaporated. The residue was chromatographed (silica gel, elution with 50% ether/hexane) to give the external enone [27 mg, (15%); ^{1}H NMR ($CDCl_3$) δ 6.5 (dt, J = 8 and 2 Hz, 1 H), 3.0–0.8 (m, 15 H); ν_{max} (film) 2960, 1720, 1645, 1460 cm^{-1}] and the internal enone [8 mg (4%); ^{1}H ($CDCl_3$) δ, 2.6–1.8 (m, 6 H), 1.9–0.8 (m, 10 H); ν_{max} (film) 2960, 1700, 1640, 1460 cm^{-1}; mass spectrum, m/e calcd 152.1201, obsd 152.1205].

Another preparation of these two compounds was to slurry aluminum chloride (201 mg, 1.5 mmol), anhydrous sodium acetate (123 mg, 1.5 mmol), and dry dichloromethane (5 mL). To this slurry, cooled to −45 °C, was added acryloyl chloride (108 mg, 1.2 mmol) followed by 4-(trimethylsilyl)hept-3-ene (202 mg, 1.19 mmol; 87% vinylsilane with the remainder being octane). The mixture was stirred in the cold for 15 min and poured into 3 M hydrochloric acid, this mixture was diluted with ether, and the phases were separated . The organic phase was extracted with a saturated solution of sodium bicarbonate, dried, and evaporated. The residue was treated at room temperature exactly as above and then heated to reflux for 12 h. The workup was performed as above. Upon chromatography, the external enone (30 mg, 19%) and internal enone (7 mg, 5%) were obtained.

Acylation with β-Chloropropionyl Chloride. 1-Acryloyl-2,5,5-trimethylcyclopentene (17). 2,2,5-Trimethylcyclopentanone was converted in the standard fashion to its benzenesulfonylhydrazone: mp 122–123 °C; 35%; ^{1}H NMR ($CDCl_3$) δ 8.0–7.2 (m, 5 H), 3.0–0.7 (series of m, 6 H), 1.12 (s, 3 H), 1.07 (d, J = 7 Hz, 3 H), 0.93 (s, 3 H). Anal. Calcd for $C_{14}H_{20}N_2O_2S$: C, 59.97; H, 7.21. Found: C, 60.16; H, 7.19.

2-(Trimethylsilyl)-1,3,3-trimethylcyclopentene (**15**) was prepared in the predescribed manner and obtained as a clear colorless liquid (45%) which was purified by preparative VPC on a 5% SE-30 column at 110 °C; ^{1}H NMR ($CDCl_3$) δ 2.4–0.4 (series of m, 4 H), 1.58 (br s, 3 H), 0.90 (s, 6 H), 0.00 (s, 9 H). Anal. Calcd for $C_{11}H_{22}Si$: C, 72.44; H, 12.16. Found: C, 72.33; H, 12.03.

To a magnetically stirred slurry of aluminum chloride (1.30 g, 9.8 mmol) in anhydrous dichloromethane (50 mL) cooled to −78 °C was added 1.11 g (12.3 mmol) of β-chloropropionyl chloride. After 5 min, the vinylsilane (1.74 g, 9.56 mmol) was added, and, after 15 min, the reaction mixture was poured into dilute hydrochloric acid (50 mL) where it was stirred for 30 min. The layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 25 mL). The combined organic layers were shaken with brine (100 mL), dried, and concentrated. The resulting amber oil (1.66 g) was passed through a plug of silica gel (7 g) with dichloromethane elution to give 1.35 g of **16**.

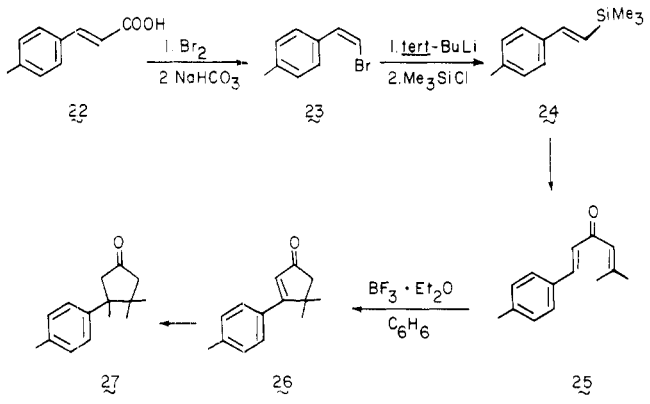
To a solution of **16** (202 mg, 1.0 mmol) in dry tetrahydrofuran (15 mL) was added 153 mg (1.0 mmol) of DBU. A precipitate was immediately deposited. The mixture was stirred at room temperature for 1 h, poured into water (50 mL), and extracted with dichloromethane (3 × 15 mL). The combined organic layers were washed with water (50 mL), dried, and concentrated. The residual brown oil (164 mg) was chromatographed on a 2 mm × 20 cm × 20 cm silica gel plate (elution with 12% ethyl acetate in hexane). There was obtained 78 mg of **17**: ^{1}H NMR ($CDCl_3$) δ 6.73–5.40 (m, 3 H), 2.53–2.10 (m, 2 H), 1.81 (br s, 3 H), 1.80–1.50 (m, 2 H), 1.20 (s, 6 H); mass spectrum m/e 164.1201, obsd 164.1204.

2,3-Dibromo-3-(4-methylphenyl)propionic Acid.[60] Bromine (10.0 g, 3.23 mL, 62.5 mmol) was added dropwise to a solution of *p*-methylcinnamic acid (10.0 g, 61.7 mmol) in chloroform (100 mL) under a nitrogen atmosphere. After several drops had been added, solid azobis(isobutylronitrile) (0.1 g) was added to initiate the reaction along with irradiation from a 150-W flood lamp. The reaction proceeded slowly with continual irradiation over 20 min. During the addition, the product crystallized from solution. The reaction mixture was stirred for an additional 10 min before

(59) Dev, S. *J. Indian Chem. Soc.* **1953**, *37*, 169.

(60) Grovenstein, E., Jr.; Lee, D. E. *J. Am. Chem. Soc.* **1953**, *75*, 2639.

Scheme V



filtration of the solid. The filtrate was concentrated to provide a second crop. The snow white crystals (16.85 g, 85%) were vacuum dried and used without further purification.

(*Z*)-1-Bromo-2-(4-methylphenyl)ethene (23).[61] 2,3-Dibromo-3-(4-methylphenyl)propionic acid (16.85 g, 52.3 mmol) and sodium bicarbonate (15.1 g, 180 mmol) were added to dry acetone (500 mL). The flask was covered with aluminum foil and heated to the reflux temperature in a darkened hood for 8 h before evaporation of the acetone. The residue was taken up in ether (300 mL), washed with water (2 × 200 mL) and brine (100 mL), and dried. The ether was evaporated to leave a residue from which the light-sensitive product could be distilled (65 °C, 0.5 torr) as a clear liquid: 9.95 g (96%); ^{1}H NMR (CCl_4) δ 7.50 (AB q, J = 8 Hz, 2 H), 7.07 (AB q, J = 8 Hz, 2 H), 6.95 (AB q, J = 8 Hz, 1 H), 6.27 (AB q, J = 8 Hz, 1 H), 2.30 (s, 3 H); mass spectrum, m/e calcd 195.9889, obsd 195.9892 (calcd for one ^{79}Br). A small forerun of acetone dimer was also collected.

(*E*)-1-(Trimethylsilyl)-2-(4-methylphenyl)ethene (24).[62] To a mixture of dry tetrahydrofuran/ether/pentane (4/1/1, 120 mL) was added (*Z*)-1-bromo-2-(4-methylphenyl)ethene (9.95 g, 50.5 mmol). The resulting solution was cooled to −120 °C (liquid nitrogen/*n*-propyl alcohol bath), whereupon a solution of *tert*-butyllithium in pentane (2 M, 50 mL, 100 mmol) was added via syringe. The mixture was mechanically stirred for 2 h before being quenched with chlorotrimethylsilane (10.85 g, 100 mmol). The mixture was allowed to warm slowly to room temperature during 16 h. The clear mixture was poured into dilute sodium bicarbonate solution, and the organic phase was separated, extracted with saturated sodium bicarbonate solution and brine, and dried. The evaporated residue was distilled [bp 42–45 °C (0.07 torr)] to give a clear liquid consisting of 70% vinylsilane **24** [2.8 g (30%); ^{1}H NMR ($CDCl_3$) δ 7.10 (AB q, J = 15 Hz, 1 H), 6.95 (br s, 4 H), 5.60 (AB q, J = 15 Hz, 1 H), 2.20 (s, 3 H), 0.0 (s, 9 H)] and 30% *p*-tolyl(trimethylsilyl)acetylene [1.2 g (13%); ^{1}H NMR ($CDCl_3$) δ 7.0 (A_2B_2 q, J = 8 Hz, 4 H), 2.20 (s, 3 H), 0.05 (s, 9 H); ν_{max} (film) 2950, 2140, 1250, and 850 cm^{-1}].

(*E*)-1-(4-Methylphenyl)-3-oxo-5-methyl-1,4-hexadiene (25). A slurry of aluminum chloride (322 mg, 2.4 mmol) in dry dichloromethane (20 mL) was cooled to −78 °C and β,β-dimethylacryloyl chloride (285 mg, 2.4 mmol) was added via syringe. To this cold slurry was added vinylsilane **24** (450 mg, 2.37 mmol). The solution which became yellow was stirred for 30 min before being poured into 3 M hydrochloric acid. This two-phase system was stirred vigorously for 15 min and diluted with ether before the layers were separated. The organic phase was extracted with water (10 mL), a saturated solution of sodium bicarbonate (10 mL), and brine (10 mL) prior to drying. The evaporated residue was pure dienone **25** in quantitative yield which could be recrystallized, with some loss of material due to extreme solubility, from hexane to give lemon-yellow crystals: mp 73.5–75 °C; ^{1}H NMR ($CDCl_3$) δ 7.5 (AB q, J = 16 Hz, 1 H), 7.4 (AB q, J = 7 Hz, 2 H), 7.1 (AB q, J = 7 Hz, 2 H), 6.7 (AB q, J = 16 Hz, 1 H), 6.3 (septet, J = 0.5 Hz, 1 H), 2.35 (s, 3 H), 2.20 (d, J = 0.5 Hz, 3 H), 1.96 (d, J = 0.5 Hz, 3 H).

3-(4-Methylphenyl)-4,4-dimethylcyclopent-2-enone (26). Dienone **25** (100 mg, 0.50 mmol) was dissolved in dry benzene (4 mL), and boron trifluoride etherate (284 mg, 2.0 mmol) was added. The yellow solution was heated to reflux for 72 h. The complex formed a red solution upon heating. The cooled solution was poured into a saturated solution of sodium bicarbonate and extracted with ether (2 × 10 mL). The organic solution was dried, evaporated, and chromatographed on silica gel (elution with 50% ether/hexane). Isolated were bands corresponding to decomposition product (R_f 0.7, 37 mg), starting dienone, (R_f 0.4, 31 mg, 31%), and desired enone **26** (10 mg, 10%, R_f 0.2): ^{1}H NMR ($CDCl_3$) δ 7.4 (A_2B_2 q, J = 8 Hz, 4 H), 6.2 (s, 1 H), 2.52 (s, 2 H), 2.44 (s, 3 H), 1.50 (s, 6 H). The spectrum was identical with that published for α,β-unsaturated ketone **26**.[58g]

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Registry No. **3**, 72233-32-0; **5**, 72245-99-9; **6**, 72233-34-2; **15**, 73839-41-5; **16**, 73855-23-9; **17**, 73839-42-6; **18**, 73839-43-7; **19**, 56975-51-0; **20**, 72233-36-4; **22**, 1866-39-3; **23**, 73839-44-8; **24**, 73839-45-9; **25**, 73839-46-0; **26**, 58812-72-9; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; cycloheptanone, 502-42-1; 4-*tert*-butylcyclohexanone, 98-53-3; 2-methylcyclohexanone, 583-60-8; 2-phenylcyclohexanone, 1444-65-1; *dl*-menthone, 1074-95-9; 4-heptanone, 123-19-3; 2-heptanone, 110-43-0; propiophenone, 93-55-0; cyclododecanone, 830-13-7; 4,5-benzocycloheptenone, 37949-03-4; α-tetralone, 529-34-0; 6-methoxy-α-tetralone, 1078-19-9; 2,2-dimethylcyclohexanone, 1193-47-1; cholestanone, 15600-08-5; cyclopentanone benzenesulfonylhydrazone, 66741-06-8; cyclohexanone benzenesulfonylhydrazone, 61892-19-1; cycloheptanone benzenesulfonylhydrazone, 61892-20-4; 4-*tert*-butylcyclohexanone tosylhydrazone, 41780-53-4; 2-methylcyclohexanone benzenesulfonylhydrazone, 56975-76-9; 2-phenylcyclohexanone benzenesulfonylhydrazone, 71445-66-4; *dl*-menthone benzenesulfonylhydrazone, 73839-47-1; 4-heptanone benzenesulfonylhydrazone, 61892-22-6; 2-heptanone tosylhydrazone, 63031-66-3; propiophenone benzenesulfonylhydrazone, 71445-63-1; cyclododecanone benzenesulfonylhydrazone, 73839-48-2; 4,5-benzocycloheptenone benzenesulfonylhydrazone, 66227-84-7; α-tetralone benzenesulfonylhydrazone, 61892-18-0; 6-methoxy-α-tetralone benzenesulfonylhydrazone, 66227-85-8; 2,2-dimethylcyclohexanone benzenesulfonylhydrazone, 73839-49-3; cholestanone benzenesulfonylhydrazone, 66227-86-9; 1-(trimethylsilyl)cyclopentene, 14579-07-8; 1-(trimethylsilyl)cyclohexene, 17874-17-8; 1-(trimethylsilyl)cycloheptene, 61892-24-8; 1-(trimethylsilyl)-4-*tert*-butylcyclohexene, 63031-67-4; 2-(trimethylsilyl)-3-methylcyclohexene, 63031-68-5; 2-(trimethylsilyl)-3-phenylcyclohexene, 73839-50-6; 2-(trimethylsilyl)-3-isopropyl-6-methylcyclohexene, 73839-51-7; (*E*)-4-(trimethylsilyl)-3-heptene, 61892-25-9; 2-(trimethylsilyl)-1-heptene, 57266-89-4; (*E*)-1-(trimethylsilyl)-1-phenylpropene, 51666-95-6; 1-(trimethylsilyl)-4,5-benzo-1,4-cycloheptadiene, 66227-89-2; 1-(trimethylsilyl)-3,4-dihydronaphthalene, 61892-23-7; 1-(trimethylsilyl)-3,4-dihydro-6-methoxynaphthalene, 66227-90-5; 2-(trimethylsilyl)-3,3-dimethylcyclohexene, 57613-55-5; 3-(trimethylsilyl)-2-cholestene, 66227-91-6; 3,3-dimethyl-3a,4,5-trihydro-2*H*-pentalen-1-one, 72233-37-5; 3,3-dimethyl-4,5,6-trihydro-2*H*-pentalen-1-one, 72233-31-9; 3,3-dimethyl-3a,4,5,6-tetrahydro-2*H*-indan-1-one, 72233-38-6; 3,3-dimethyl-3a,4,5,6-tetrahydro-2*H*-indan-1-one 2,4-dinitrophenylhydrazone, 73839-52-8; 3,3-dimethyl-4,5,6,7-tetrahydro-2*H*-indan-1-one, 30434-75-4; 3,3-dimethyl-4,5,6,7-tetrahydro-2*H*-indan-1-one 2,4-dinitrophenylhydrazone, 30434-76-5; 3,3-dimethyl-3a,4,5,6,7-pentahydro-2*H*-azulen-1-one, 72233-40-0; 3,3-dimethyl-4,5,6,7,8-pentahydro-2*H*-azulen-1-one, 72233-41-1; 15,15-dimethylbicyclo[10.3.0]pentadec-11-en-13-one, 72233-42-2; 15,15-dimethylbicyclo[10.3.0]pentadec-12-en-13-one, 72233-43-3; 2-propylidene-3-ethyl-4,4-dimethylcyclopentanone, 73839-53-9; 2-propyl-3-ethyl-4,4-dimethylcyclopentenone, 72233-44-4; 3,3,7-trimethyl-3a,4,5,6-tetrahydro-2*H*-indan-1-one, 72233-45-5; 3,3,7-trimethyl-4,5,6,7-tetrahydro-2*H*-indan-1-one, 72233-39-7; 3-methyl-4,5,6-trihydro-2*H*-pentalen-1-one, 2146-42-1; 3-methyl-4,5,6-trihydro-2*H*-pentalen-1-one 2,4-dinitrophenylhydrazone, 73855-20-6; 3-methyl-4,5,6,7-tetrahydro-2*H*-indan-1-one, 18631-68-0; 3-methyl-4,5,6,7-tetrahydro-2*H*-indan-1-one 2,4-dinitrophenylhydrazone, 73855-21-7; 3,3a,4,5,6-pentahydro-2*H*-indan-1-one, 40954-63-0; 3,4,5,6,7-pentahydro-2*H*-indan-1-one, 22118-00-9; 2-propylidene-3-ethylcyclopentanone, 73839-54-0; 2-propyl-3-ethylcyclopent-2-enone, 13679-31-7; 3,4,5,6,7,8-hexahydro-2*H*-azulen-1-one, 769-32-4; 2-methylcyclopentanone, 1120-72-5; 2-methylcyclopentanone benzenesulfonylhydrazone, 73839-55-1; *exo-cis*-4,4,8-trimethylbicyclo[3.3.0]octan-2-

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one, 2737-36-2; *endo-cis*-4,4,8-trimethylbicyclo[3.3.0]octan-2-one, 10067-57-9; *exo-cis*-4,8-dimethylbicyclo[3.3.0]oct-3-en-2-one, 5260-84-4; 2,2,5-trimethylcyclopentanone, 4573-09-5; 2,2,5-trimethylcyclopentanone benzenesulfonylhydrazone, 73839-56-2; 2,3-dibromo-3-(4-methylphenyl)propionic acid, 52916-86-6; *p*-tolyl(trimethylsilyl)acetylene, 4186-14-5; β,β-dimethylacryloyl chloride, 3350-78-5; crotonyl chloride, 10487-71-5; acryloyl chloride, 814-68-6; β-chloropropionyl chloride, 625-36-5.

Silanes in Organic Synthesis. 9. Enesilylation as a Method for 1,2-Carbonyl Migration within Ketones and for Conversion to 1,2-Transposed Allylic Alcohols[1]

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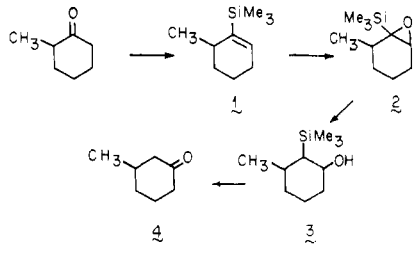
Vinylsilanes are shown to be valuable synthetic intermediates in useful transformations of ketones. The epoxidation of vinylsilanes followed by lithium aluminum hydride reduction and oxidation with chromic acid and sulfuric acid in a two-phase (ether/water) system often gives high yields of 1,2-transposed ketones. With singlet oxygen and sequential sodium borohydride reduction, 2-trimethylsilyl alcohols are produced in which the α position of the parent ketone has been regiospecifically oxygenated. Fluoride ion promoted desilylation completes the conversion to the migrated allylic alcohol.

The carbonyl group is pivotal in bringing latitude to organic synthesis. The need to relocate this functional group within a molecule occurs with sufficient frequency that interest in efficient methods of carbonyl transposition remains high. Various procedures have been developed for effecting site exchange within saturated[4-13] and α,β-unsaturated ketones,[14-17] sometimes in tandem with an alkylation step,[18-20] and these have met with varying degrees of accepted usage. In this paper, we describe a quite different approach to the 1,2-transposition of ketones which takes advantage of the chemical properties associated with covalently bonded silicon.[21] Also described herein is a simple procedure which shifts the position of a ketone carbonyl in an entirely predictable manner with simultaneous introduction of a double bond.[22] Little known α-silylated allylic alcohols and ketones result, and these substances serve as precursors to the silicon-free end products. The high regioselectivity of these novel functionality-transposing reactions suggests that they may hold considerable importance in organic synthesis.

Scheme I



1,2-Keto Transposition. In the accompanying paper, it was demonstrated that vinyl carbanions, generated through reaction of ketone arenesulfonylhydrazones with alkyllithium reagents in tetramethylethylenediamine solution, react with chlorotrimethylsilane to deliver vinylsilanes in excellent yield. Where relevant, this transformation is regiospecific, deprotonation occurring preferentially for electronic and steric reasons at the less substituted α position. With the introduction of such unsaturation comes the further possibility of functionalizing the carbon atom β to silicon. This phenomenon provides for the possibility of vinylsilane-mediated oxygen transposition.

The methodology envisioned for the 1,2-carbonyl relocation is illustrated in Scheme I. Epoxidation of 1 to give

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