The observed vicinal isotope shifts are additive, within the experimental error. The shift of the axial fluorine in the d_4 compound (**9**, 1.06 ± 0.03 ppm) compares well with the sum of two axial–axial and two axial–equatorial shifts (0.98 ± 0.11). The shift of the equatorial fluorine in **10** (0.60 ± 0.03) is close to the sum of two equatorial–equatorial and two equatorial–axial shifts (0.66 ± 0.07). This near additivity contrasts with observations in a geminal series, CH_4, CDH_3, CD_2H_2, CD_3H, in which the isotope shifts for the last three compounds are 0.019, 0.027, and 0.045 ppm.[12] It is therefore not valid at this point to generalize from our vicinal ^{19}F isotope shifts to other cases, such as these smaller geminal ^1H shifts.

Acknowledgment. This work was supported by the National Science Foundation (Grants GP-34259X and GP-35868X).

(12) R. A. Bernheim and B. J. Lavery, *J. Chem. Phys.*, **42**, 1464 (1965).

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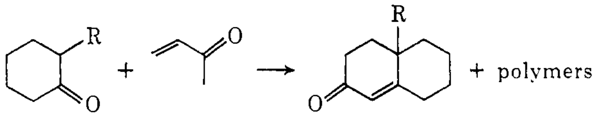
Received June 1, 1973

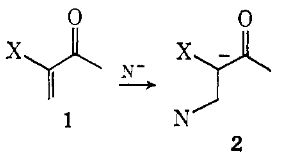
α-Silylated Vinyl Ketones. A New Class of Reagents for the Annelation of Ketones

Sir:

The annelation of 2-alkylcyclohexanones with methyl vinyl ketone and its homologs is an important route to fused polycyclic systems.[1] While condensation at the less substituted α carbon can be carried out efficiently using the corresponding enamines,[2] the conditions required for reaction at the more substituted site result in polymerization of the vinyl ketone and generally low yields.[3] This type of difficulty is avoided by the use of alkyl halides instead of vinyl ketones[4] but a number of steps are then required to transform the added alkyl group into the desired 3-ketoalkyl function.



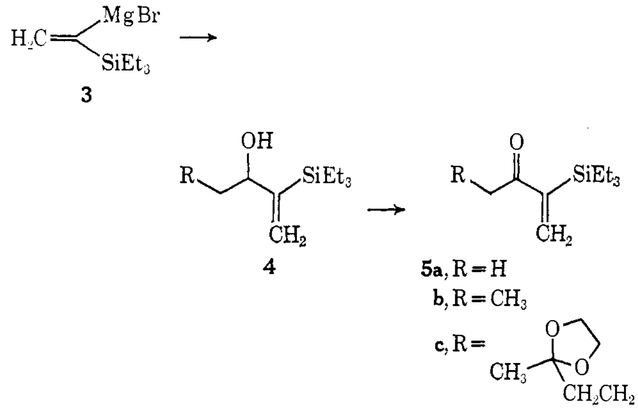
The problem with simple vinyl ketones, such as methyl vinyl ketone, comes from the similar base strengths and reactivities of the enolate ions derived from the starting material and the Michael adduct. We have therefore looked into the possibility of designing stable α-substituted vinyl ketones of type **1**, in which the substituent X would be capable of stabilizing the enolate **2** resulting from 1,4 addition. At the same time X must be easily removed, *e.g.*, during the subsequent cyclization of the adduct.



1 **2**

There is good evidence that silicon, with its vacant 3d orbitals, can stabilize an adjacent negative charge.[5] We wish to report here the synthesis of silylated vinyl ketones such as **1** (X = R_3Si) and illustrate their use in the annelation of certain ketone enolates.

The Grignard reagent **3**, prepared in the usual fashion from α-bromovinyltriethylsilane,[6] reacted with excess acetaldehyde to form **4a** in 80% yield: nmr δ 5.95 (m, 1 H), 5.30 (d, 1 H, J = 2 Hz), 4.35 (br s, 1 H), 1.20 (d, 3 H, J = 7 Hz), 0.4–1.2 (m, 15 H). This allylic alcohol was readily oxidized by Jones reagent to the enone **5a**: bp 83° (7 mm); nmr δ 6.58, 6.11 (AB quartet, J = 2 Hz), 2.15 (s, 3 H), 0.4–1.2 (m, 15 H); ir 5.99 μ; mass spectrum m/e 184 (M^+).[7]



3

4

5a, R = H
b, R = CH_3
c, R =

In a similar fashion, the corresponding vinyl ketones **5b** (bp 100° (7 mm)) and **5c** were prepared from propionaldehyde and 5-ethylenedioxyhexanal,[8,9] respectively. Besides being pleasant-smelling liquids, these α-silylated vinyl ketones could be distilled with virtually no decomposition and proved to be stable for months at −20°.

We have made the important observation that α-silylated enones can participate in Michael addition under *aprotic conditions*. These are, of course, the conditions which lead to maximum polymerization with methyl vinyl ketone itself. The lithium enolate of cyclohexanone (generated in tetrahydrofuran from its enol silyl ether, using methyllithium)[10] was treated with 1 equiv of **5a** at −78° and the solution was then allowed to reach room temperature; this led to the adduct **6** in high yield.[11] The validity of the approach

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(1) For a good review see E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. React.*, **10**, 179 (1959).

(2) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).

(3) J. A. Marshall and W. I. Fanta, *J. Org. Chem.*, **29**, 2501 (1964), and references cited therein.

(4) G. Stork, S. Danishefsky, and M. Ohashi, *J. Amer. Chem. Soc.*, **89**, 5459 (1967); G. Stork, S. Uyeo, T. Wakamatsu, P. Grieco, and J. Labovitz, *J. Amer. Chem. Soc.*, **93**, 4945 (1971).

(5) Vinyltriarylsilanes, for example, readily add organolithium reagents: (a) L. F. Cason and H. G. Brooks, *J. Amer. Chem. Soc.*, **74**, 4582 (1952); (b) L. F. Cason and H. G. Brooks, *J. Org. Chem.*, **19**, 1278 (1954). Also, tetramethylsilane has recently been metalated: (c) D. J. Peterson, *J. Organometal. Chem.*, **9**, 373 (1967).

(6) Prepared by the method of A. Ottolenghi, M. Fridkin, and A. Zilkha, *Can. J. Chem.*, **41**, 2977 (1963).

(7) This substance was obtained pure only by preparative gas chromatography. The crude distilled product could be used in annelations.

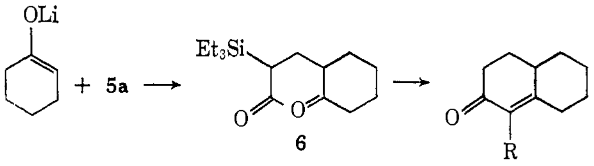
(8) This aldehyde was prepared by reduction of the corresponding nitrile with diisobutylaluminum hydride. The silyl vinyl ketone **5c** was purified by silica gel chromatography using benzene.

(9) Nmr, ir, and mass spectral data are consistent with the proposed structure.

(10) G. Stork and P. F. Hudrlik, *J. Amer. Chem. Soc.*, **90**, 4462, 4464 (1968); H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969).

(11) By comparison, the reaction of methyl vinyl ketone under identical conditions gave less than 5% of material arising from 1,4 addition.

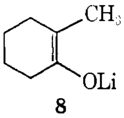
had thus been demonstrated, but for the activating group to be of practical value, it must be easily removed, and we expected cleavage of the triethylsilyl moiety during completion of the annelation process. Indeed, heating the crude adduct **6** in 5% sodium methoxide–methanol afforded $\Delta^{1,9}$-2-octalone **7a** in an overall yield of 80%.[12] The use of **5b** in the annelation reaction similarly led to the octalone **7b** in ~70% yield.



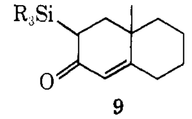
6

7 a, R=H
b, R=CH$_3$

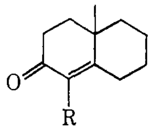
With 2-methylcyclohexanone, conjugate addition at the more substituted position could be carried out either using the pure lithium enolate **8**, derived from the silyl ether, or more simply by mixing equimolar amounts of annelating agent **5a** and 2-methylcyclohexanone in *tert*-butyl alcohol containing a catalytic amount of potassium *tert*-butoxide. This latter technique afforded primarily the silylated enone **9** which was easily transformed into the known methyloctalone **10a** (60% yield by vpc calibration, using **10a** as a standard) by boiling with sodium hydroxide–isopropyl alcohol solution.[12] Reaction of the lithium enolate **8** with the silylated enone **5b** similarly gave the octalone **10b** in ~60% yield.



8

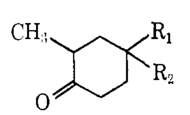


9

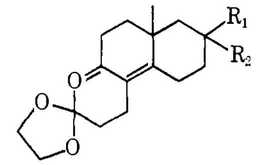


10a, R=H
b, R=CH$_3$

α-Silyl vinyl ketones such as **5c** allow the preparation of highly functionalized octalones such as **12a–c** in good yields. The following represents a typical experimental procedure. A solution of **11b** (1.2 g, 7 mmol,[13] in *tert*-butyl alcohol) (15 ml) was treated with the enone **5c** (2.25 g, 7 mmol, in 10 ml of *tert*-butyl alcohol) at room temperature under an inert atmosphere. Later (2.5 hr), the deep red solution was poured into ether (150 ml) and washed successively with water and brine. After drying and concentration, the crude product was taken up in 10% aqueous sodium hydroxide (6 ml) and isopropyl alcohol (9 ml) and then refluxed for 12 hr. Ether extraction afforded a dark oil which was heated under vacuum in a Kugelrohr oven at 120° (0.2 mm) to remove triethylsilanol. Column chromatography of the residue furnished 1.7 g (73%) of **12b** as a clear oil.[8]



11



12a, R$_1$=R$_2$=H
b, R$_1$, R$_2$=OCH$_2$CH$_2$OH
c, R$_1$, R$_2$=CH$_2$=

The contrast with the classical method is worth emphasizing. For instance, condensation as just described of **8** with the silylated enone **5c** led in about 70% yield to **12a**. On the other hand we were unable to isolate any enone **12a** from the condensation of 2-methylcyclohexanone with the unsilylated analog of the vinyl ketone **5c** in the presence of potassium *tert*-butoxide–*tert*-butyl alcohol, conditions which had proved very satisfactory for the synthesis of **10a** from methylcyclohexanone and the silylated enone **5a**.

The feasibility of carrying Michael additions under aprotic conditions, by the use of silylated vinyl ketones, is a step forward. Nevertheless, the method presented here is not suitable at the present time for the trapping of kinetically generated, *regio-unstable*, lithium enolates because they equilibrate faster (*via* proton transfers) than they undergo Michael addition. In such situations alkylation with reactive halides is, of course, a feasible alternative.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for their support of this investigation.

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Received June 22, 1973

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[12] This material was shown to be identical with an authentic sample, prepared by published procedures.

[13] S. A. Narang and P. C. Dutta, *J. Chem. Soc.*, 2842 (1960).

*Book Reviews**

Crystal Data Determinative Tables. Third Edition. Volume I: Organic Compounds. Volume II: Inorganic Compounds. Edited by J. D. H. Donnay and H. M. Ondik. U. S. Department of Commerce, National Bureau of Standards, and the Joint Committee on Powder Diffraction Standards, Swarthmore, Pa. 1972 and 1973. Vol. I: ix + 865 pp. \$30.00. Vol. II: ix + 2106 pp. \$50.00.

The previous edition of this important work of reference appeared in 1963 and 1967, and the number of entries has increased from 13,000 to 24,000. An impressive international group of crystallographers compiled the data, which for the first time have been placed on magnetic tape to make possible computer searches. The editors express the hope that having the data on tape will also facilitate preparing later editions, and particularly to reduce the time lag (six years for this edition!) between the end of literature coverage and publication. Entries are arranged according to crystal type, but formula, chemical name, and mineral name indexes facilitate manual access to particular data.

Determination of Organic Structures by Physical Methods. Volume 5. Edited by F. C. Nachod and J. J. Zuckerman. Academic Press, New York, N. Y. 1973. xv + 367 pp. \$26.00.

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* Unsigned book reviews are by the Book Review Editor.