ometry. Structure 2 is now higher in energy than either 1 or 3. Although a complete geometry optimization in this larger basis was not feasible, two cycles of the gradient procedure increased the energy difference between structure 1 and 3 to 1.95 kcal/mol.

The energy differences between the various enolate structures are small and could be modified by solvent effects which are neglected in our calculations. In addition, simple enolates probably exist as aggregates which can vary in average size as a function of solvent or concentration.[13] Nevertheless, the conclusion that chiral enolates are low-energy structures is important as a guide for future study in asymmetric syntheses involving chiral nucleophiles. This conclusion suggests that enolates containing internal ligands may be prepared such that a new chiral center would exist by virtue of the counterion position. A recent structure of a substituted lithium phenoxide dimer provides an example of a potentially chiral π-stabilized lithium–oxygen species which has some structural similarities to the chiral species 2 we describe above.[14] Our proposal finds further precedent in some recent work by Posner in which an internal arene was postulated to act as a ligand for an out-of-plane lithium in some cyclic enolates.[15] Topological arguments for out-of-plane lithium have also been at least implied in speculation about the basis of some successful asymmetric syntheses.[16] From the results of our calculations, we believe these are the very sort of lithium enolates likely to have an even stronger preference for an out-of-plane lithium than the acetaldehyde enolate and that further studies of lithio enolates may lead to unambiguous demonstration of a chiral lithium enolate.

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Registry No. Lithium acetaldehyde enolate, 2180-63-4.

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[13] Jackman, L. M.; Szeverenyi, N. M. *J. Am. Chem. Soc.* **1977**, *99*, 4954.

[14] The structure of lithium 2,6-di-*tert*-butylphenoxide, which was recently reported, is achiral only by virtue of the high symmetry of the phenoxide ligands: Cetinkaya, B.; Gumrukcu, I.; Lappert, M. F.; Atwood, J. L.; Shakir, R. *J. Am. Chem. Soc.* **1980**, *102*, 2088.

[15] Posner, G. H.; Lentz, C. M. *J. Am. Chem. Soc.* **1979**, *101*, 934.

[16] Meyers, A. I.; Whitten, C. E. *Heterocycles* **1976**, *4*, 1687. Davenport, K. G.; Eichenauer, H.; Enders, D.; Newcomb, M.; Bergbreiter, D. E. *J. Am. Chem. Soc.* **1979**, *101*, 5654.

Communications

Preparation of a Terminal Allene, 3-Haloallene, and 3-Acylallene from a Propargyltrimethylsilane

Summary: Preparations of a terminal allene, 3-haloallene, and 3-acylallene from the reaction of a propargyltrimethylsilane with trifluoroacetic acid, bromine or iodine, and acetyl chloride–aluminum chloride, respectively, are reported.

Sir: Recently the previously little-studied propargyltrimethylsilanes have become readily accessible from the reaction of the lithium salts of alkynes with (trimethylsilyl)methyl halides[1] or triflate (trifluoromethanesulfonate)[1,2] (eq 1). In a reaction comparable to reactions

(1)

of allylsilanes,[3] a propargylsilane containing a tosylate initiator has recently been shown to undergo an intramolecular electrophilic cyclization to give a five-membered ring having an exocyclic allene group.[2] Importantly, a similar reaction has now been utilized in Johnson's laboratory to form ring D of a steroid precursor.[4]

On the contrary, propargyltrimetylsilane did not give a $TiCl_4$-catalyzed reaction with adamantyl chloride under conditions where allyltrimethylsilane gave the typical carbon–carbon bond formation with concomitant double bond shift.[5] Reactions of $(CH_3)_3SiC{\equiv}CCH_2Si(CH_3)_3$ with electrophiles Br_2, SO_3, $MeSO_3H$, and $ClSO_3SiMe_3$ did give some expected products of electrophilic attack with cleavage of Si.[6a,b] A comparable reaction of acetals was very recently reported.[6c]

We have explored the reactions of propargyltrimethylsilanes with several electrophiles and with NaOEt to give the results shown in Scheme I. Of particular interest in Scheme I is the reaction with the electrophile, H^+, which gave, after distillation, pure allene 2 in moderate yield. This reaction, in conjunction with our propargylsilane preparation, constitutes a convenient *two-step preparation of a terminal allene from the terminal alkyne having one fewer carbon atoms.* Presently, such allenes are preparable from the alkene having one fewer carbon atoms through reaction with dibromocarbene, followed by an alkyllithium,[7a] or from an aldehyde having two fewer carbon atoms by reaction with α-silylvinyl carbanions followed by subsequent transformations.[7b]

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[1] Chiu, S. K.; Peterson, P. E. *Tetrahedron Lett.*, in press.

[2] Despo, A. D.; Chiu, S. K.; Flood, T.; Peterson, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 5121.

[3] Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.

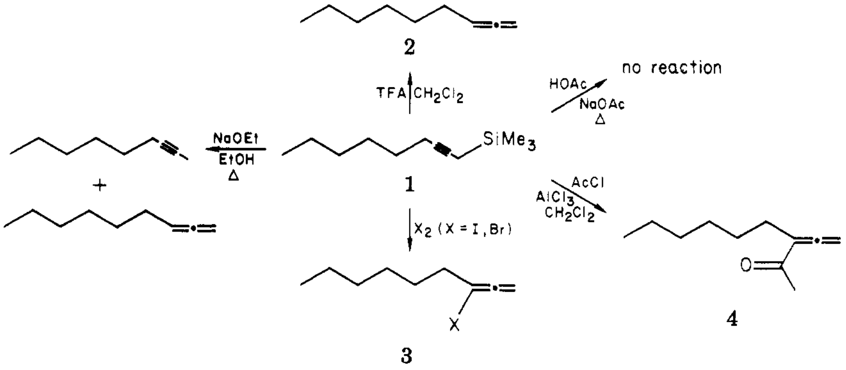
[4] Schmid, R.; Huesman, P. L.; Johnson, W. S. *J. Am. Chem. Soc.* **1980**, *102*, 5122. We thank Professor Johnson for a preprint of this paper.

[5] Sasaki, T.; Usuki, A.; Ohno, M. *Tetrahedron Lett.* **1978**, 4925.

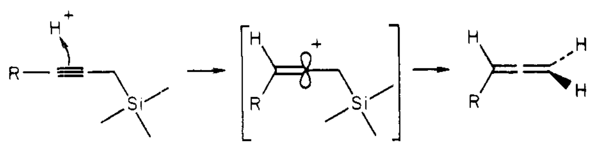
[6] (a) Bourgeois, P.; Merault, G. *C. R. Hebd. Seances Acad. Sci., Ser. D* **1971**, *273*, 714. (b) Bourgeois, P.; Merault, G. *J. Organomet. Chem.* **1972**, *39*, C44. (c) Pornet, J. *Tetrahedron Lett.* **1980**, 2049.

[7] (a) Taylor, D. R. *Chem. Rev.* **1967**, *67*, 317. (b) Chan, T. H.; Mychajlowskij, W.; Ong, B. S.; Harp, D. N. *J. Org. Chem.* **1978**, *43*, 1526.

Scheme I



Although the acid cleavage of propargylsilanes (like other electrophilic reactions) is expected to be facilitated by β-silicon stabilization of a cationic transition state (eq 2), the silanes survive moderately acidic conditions (glacial HOAc, 75 °C, 17 h, our study) of 10% aqueous HCl–THF.[4] However, in methylene chloride and trifluoroacetic acid (1.1 equiv) at room temperature, reaction occurred very rapidly (<1 h) to give, after distillation, pure 1,2-nonadiene:[8] bp 50 °C (20 mmHg); GC yield, 60%; distilled yield, 52%; ^{1}H NMR δ 5.10 (m, 1 H, RCH=), 4.66 (m, 2 H =CH$_2$); ^{13}C NMR δ 208.5 (C=**C**=C), 89.3, 73.7 (allenic carbons); IR 1957 cm^{-1} (C=C=C).



(2)

On the basis of data mentioned below, the reaction of iodine or bromine with the propargyltrimethylsilane gave the 3-haloallene (3, Scheme I). *Surprisingly, our literature search indicates that pure 3-haloallenes have not been previously prepared.* Only one example, 3-chloro-1,2-butadiene obtained as a component of a mixture by isomerization of 1-chloro-2-butyne seems to have been reported.[9] By comparison with the 1-haloallenes[10] the 3-haloallenes are expected to be less reactive in S$_N$1 or S$_N$2 reactions than the corresponding allylic halides. The reactions of 1-(trimethylsilyl)-2-nonyne with I$_2$ or Br$_2$ (CH$_2$Cl$_2$, –78 °C) gave products having triplets (J = 3 Hz) near 4.55 ppm. Only the bromination product was isolable in its pure form (yield 58%, bp 44–46 °C (0.05 torr), from 3.9 g of reactant) and was shown to be 3-bromo-1,2-nonadiene (Scheme I) by NMR and IR: ^{1}H NMR δ 4.83 (t, 2 H, =CH$_2$); ^{13}C NMR δ 204.2 (C=**C**=C), 93.0 (BrC=C=), 80.9 (=C=CH$_2$); IR 1960 cm^{-1} (surprisingly weak, C=C=C). Mass spectroscopy showed bromine-containing fragments, including m/e 132 and 134 attributable to CH$_2$=CBrCH–CH$_2^+$, previously observed for an ω-haloallene.[11] Impurity peaks in the ^{13}C NMR spectrum were less than 5% of the height of CH$_2$ peaks. Elemental analysis was not attempted owing to evidence of instability upon storage.

Acetylation of the propargyltrimethylsilane 1 occurred with cleavage of silicon to give 3-alkyl-3-acylallene (or ethenylidene ketone) (4, Scheme I). Such compounds have been prepared from species which may be regarded as anions having propargyl and allenic resonance forms.[12] As might be anticipated, these preparations usually give mixtures. Our material showed no evidence for the presence of isomers in the ^{13}C NMR spectrum. Our procedure is described below. Addition of a mixture of aluminum trichloride (0.83 g, 0.0012 mol), methylene chloride (4.5 mL), and acetyl chloride (0.46 g, 0.0059 mol) to a solution of 1-(trimethylsilyl)-2-nonyne (1.15 g, 0.0058 mol) in methylene chloride (5 mL) at –78 °C gave, after stirring for 45 min at –78 °C followed by warming to room temperature and workup with saturated NaHCO$_3$, the expected product, 3-acetyl-1,2-nonadiene, in 3% yield after distillation: ^{1}H NMR δ 5.18 (t); ^{13}C NMR δ 216.9 (C=C=C), 198.5 (C=O), 109.2, 79.3 (allenic carbons); IR 1970 (C=C=C), 1685 (C=O) cm^{-1}. Since there was evidence of instability upon storage, an elemental analysis was not attempted.

In analogy with reactions of allylsilanes, reactions of (trimethylsilyl)-2-nonyne with acetone and TiCl$_4$[13] and with *tert*-butyl chloride and TiCl$_4$ or AlCl$_3$[14] were attempted. We failed to obtain products analogous to those formed from allylsilanes. The major products, after workup, were 1,2-nonadiene and unidentified materials.

Since the base reactions of propargylsilanes are little known, we refluxed a solution of (trimethylsilyl)-2-nonyne and sodium ethoxide (1:2 mole ratio) in ethanol for 48 h and found it to yield 2-nonyne and 1,2-nonadiene in a ratio of approximately 1.5:1.00 (by ^{1}H NMR integration).

In summary, several interesting functionalities are now accessible in two steps from terminal acetylenes via propargylsilanes.

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Registry No. 1, 74581-76-3; 2, 22433-33-6; 3 (X = Br), 75101-95-0; 4, 75111-00-1; 2-nonyne, 19447-29-1.

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(8) Skattebol, L. *Acta Chem. Scand.* **1963**, *17*, 1683.

(9) Mkryan, G. M.; Papazyan, N. A.; Arsenyan, G. B.; Avetisyan, E. A.; Zhurba, V. F.; Nazaryan, A. A. *Zh. Org. Khim.* **1971**, *7*, 2466; *J. Org. Chem. USSR* (*Engl. Transl.*) **1971**, *7*, 2562.

(10) (a) Black, D. K.; Landor, S. R.; Patel, A. N.; Whiter, P. F. *Tetrahedron Lett.* **1962**, 483. (b) Baker, C. S. L.; Landor, P. D.; Landor, S. R.; Patel, A. N. *J. Chem. Soc.* **1965**, 4348. (c) Simo, M. S.; Jean, A.; Lequan, M. *J. Organomet. Chem.* **1972**, *35*, C23. (d) Jacobs, T. L.; Petty, W. L. *J. Org. Chem.* **1963**, *28*, 1360. (e) Shiner, V. J.; Wilson, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 2402.

(11) Arseniyadis, S.; Gore, J.; Roumestant, M. L. *Org. Mass Spectrom.* **1978**, *31*, 54.

(12) (a) Couffignal, R.; Guademar, M. *Bull. Soc. Chim. Fr.* **1969**, 898. (b) Gelin, R.; Gelin, S.; Deshayes, C. *Ibid.* **1973**, 3163.

(13) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1295.

(14) Fleming, I.; Paterson, I. *Synthesis* **1979**, 445.