NMR ($CDCl_3$) δ 6.80–6.50 (3 H, m), 3.77 (3 H, s), 3.60 (1 H, m), 3.14 (3 H, s), 3.40–2.90 (4 H), 2.4–1.0 (15 H, and 1 H exch D_2O). Noteworthy, is the observation that the broad signal at δ 3.60 becomes a sharp doublet of doublets upon D_2O shake. This pattern is typical for H-2 of Aspidosperma alkaloids and is indicative of the correct stereochemistry.[4,5] Treatment of **19** with propionyl chloride–pyridine (4 equiv) in benzene afforded *O,O*-dimethyllimaspermine (**20**), mp 162–163.5 °C, which now showed the characteristic doublet of doublets (J = 9 and 6 Hz) for H-2 at δ 4.56 in the NMR spectrum, again indicative of the correct stereochemistry. We have carried out preliminary studies on the deprotection of the methyl ether group of **20** which are encouraging. Thus, treatment of **20** with iodotrimethylsilane ($CHCl_3$, C_5H_5N, 60 °C, 21 h) afforded a low yield (ca. 25%) of limaspermine (**4**), having IR and mass spectra in agreement with those of the natural product,[2] together with unreacted **20**. Treatment of the dimethyl ether with BBr_3 (4.4 equiv, CH_2Cl_2, −78 °C, then 20 °C, 17 h) gave a low yield of limaspermine monomethyl ether **21**, together with unreacted **20**. No other alkaloid products were evident from these reactions.

Since the above sequence is relatively long, we have not undertaken further deprotection studies of **17**, but instead we have diverted our attention to a more flexible and efficient synthesis of the intermediate **16**, based on methodology we recently developed[12] for a preparation of Stork's aspidospermine intermediate **22**. The work described here establishes a precedent for the application of functionalized tricarbonyldienyliumiron complexes to the total synthesis of nontrivial natural product molecules.

Acknowledgment. We are grateful to the S.E.R.C. and I.C.I. Pharmaceuticals Limited for financial support.

---

(12) Pearson, A. J. *Tetrahedron Lett.* **1981**, 4033.

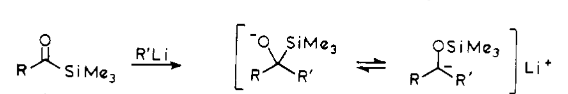
Silyl Ketone Chemistry.[1] Synthesis and Reactions of Olefinic and Acetylenic Silyl Ketones

Hans J. Reich* and Martha J. Kelly

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received November 13, 1981

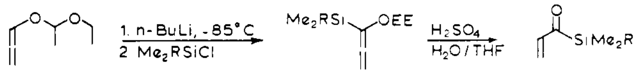
The reaction of organolithium reagents with silyl ketones (**1**) gives siloxy carbanions (**2**), valuable synthetic intermediates for the preparation of enol, dienol, and allenol silyl ethers.[1,2] The full potential of this methodology cannot be explored without convenient syntheses of silyl ketones with varied substituents R. We report here successful routes to previously unknown or poorly accessible silyl ketones having α,β-olefinic, α,β-acetylenic, and α-keto functions (**1**, R = vinyl, alkynyl, and acyl) and on some of their chemistry.



1

2

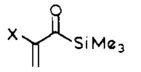
Vinyl silyl ketones have been prepared by several methods[1b,2d,3] of which the one reported by Leroux and co-workers[3a] seemed to us to be suitable for more general application.[3b] The procedure we have developed uses as starting material the alkoxyallene **3**, readily available from propargyl alcohol.[4] Deprotonation of **3** and silylation gave silanes **4a** and **4b**[5] (throughout this paper the a series refers to trimethylsilyl and the b to *tert*-butyldimethylsilyl). These compounds are key intermediates for the preparation of a whole family of new silyl ketones. Hydrolysis of **4** (0.2 N H_2SO_4 in 10% aqueous THF) gave the yellow silyl enones **5a**[6a] and **5b**, whereas reaction with other electrophiles such as sulfuryl chloride or benzeneselenenyl chloride (CH_2Cl_2, −78 °C) gave the α-substituted enones **6a** and **7a**.[1a,3b] Oxidation of **4** under carefully controlled conditions[7] gave the deep red α-dicarbonyl compound **8**.[6b]



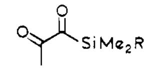
3

4a R = Me 86%
b R = t-Bu 78%

5a 65%
b 84%

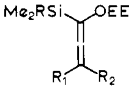


6a X = Cl 65%
7a X = SePh 73%

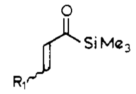


8a 42%
b 90%

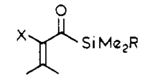
The silylallenes **4** can be subjected to additional metalations followed by reaction with electrophiles to produce new allenes having one or two γ substituents (**9**).[8] Hydrolysis or bromination (Br_2, CH_2Cl_2, −78 °C) of these allenes leads to a series of silyl enones, some representative examples of which are shown. Yields in each case are based on compound **4**. Only one of these substances (**10a**) has been prepared previously.[3e]



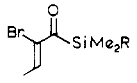
9



R_1 = SePh 79%
R_1 = $SiMe_3$ 64%



10a X = H 68%
11a X = Br 70%
b X = Br 76%



R = t-Bu 67%

We have also been successful in using **5** to synthesize the first α,β-acetylenic silyl ketones **12b** and **13b**. The triple bond is formed

---

(1) Previous papers in this series: (a) Reich, H. J.; Rusek, J. J.; Olson, R. E. *J. Am. Chem. Soc.* **1979**, *101*, 2225. (b) Reich, H. J.; Olson, R. E.; Clark, M. C. *J. Am. Chem. Soc.* **1980**, *102*, 1423.

(2) For other synthetic applications of silyl ketones (acylsilanes) see: (a) Kuwajima, I.; Kato, M. *J. Chem. Soc., Chem. Commun.* **1979**, 708. *Tetrahedron Lett.* **1980**, *21*, 623. (b) Kuwajima, I.; Atsumi, K.; Tanaka, T.; Inoue, T. *Chem. Lett.* **1979**, 1239. (c) Schinzer, D.; Heathcock, C. H. *Tetrahedron Lett.* **1981**, 1881. (d) Miller, J. A.; Zweifel, G. *J. Am. Chem. Soc.* **1981**, *103*, 6217. (e) Degl'Innocenti, A.; Pike, S.; Walton, D. R. M.; Seconi, G.; Ricci, A.; Fiorenza, M. *J. Chem. Soc., Chem. Commun.* **1980**, 1201.

(3) (a) Leroux, Y.; Roman, C. *Tetrahedron Lett.* **1973**, 2585. Leroux, Y.; Mantione, R. *Ibid.* **1971**, 591. *J. Organomet. Chem.* **1971**, *30*, 295. (b) Conversion of methoxyallene to a silyl enone: Clinet, J.-C.; Linstrumelle, G. *Tetrahedron Lett.* **1980**, 3987. (c) Reich, H. J.; Shah, S. K. *J. Am. Chem. Soc.* **1977**, *99*, 263. (d) Reich, H. J.; Shah, S. K.; Gold, P. M.; Olson, R. E. *Ibid.* **1981**, *103*, 3112. (e) Hassner, A.; Soderquist, J. A. *J. Organomet. Chem.* **1977**, *131*, C1. Soderquist, J. A.; Hassner, A. *J. Am. Chem. Soc.* **1980**, *102*, 1577. (f) Minami, N.; Abe, T.; Kuwajima, I. *J. Organomet. Chem.* **1978**, *145*, C1.

(4) Hoff, S.; Brandsma, L.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 916. For some recent applications of lithiomethoxyallene:[3b] Gange, D.; Magnus, P. *J. Am. Chem. Soc.* **1978**, *100*, 7746 and references therein. Miyaura, N.; Yoshinari, T.; Itoh, M.; Suzuki, A. *Tetrahedron Lett.* **1980**, *21*, 537. Oostveen, J. M.; Westmijze, H.; Vermeer, P. *J. Org. Chem.* **1980**, *45*, 1158.

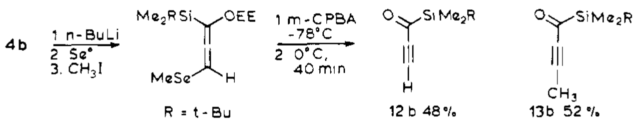
(5) The silylation with t-$BuMe_2SiCl$ was carried out in Et_2O, HMPA (1.6 equiv), −85 °C, 15 h.

(6) All new compounds showed IR, NMR, and mass spectra consistent with the structures assigned. Some representative data are as follows. **5a**: NMR δ 0.08 (s, 9 H), 5.76, 5.88 (dd, J = 10, 2 Hz; dd, J = 18, 2 Hz, 2 H), 6.28 (dd, J = 18, 10 Hz, 1 H); ^{13}C NMR δ -2.5 (q), 127.7 (t), 141.0 (d), 236.7 (s); IR 1641, 1604 cm^{-1}; UV (cyclohexane) λ_{max} (ϵ) 434 (96.4), 213 (8630); MS, M^+ 128.0656 (Calcd 128.06577). (b) **8a**: NMR δ 0.13 (s, 9 H), 2.03 (s, 3 H); IR 1713, 1658 cm^{-1}; ^{13}C NMR δ -2.9, 21.5, 199.2, 235.5; UV (cyclohexane) λ_{max} (ϵ) 535 (99), 296 (41), 285 (40). (c) **13b**: NMR δ 0.10 (s, 6 H), 0.87 (s, 9 H), 2.05 (s, 3 H); ^{13}C NMR δ -7.5, 4.3, 16.7, 26.3, 85.0, 98.2, 225.7; IR 2200, 1731, 1605 cm^{-1}; UV (cyclohexane) λ_{max} (ϵ) 420 (170), 227 (7450). (d) **18b**: NMR δ 0.07 (s, 6 H), 0.89 (s, 9 H), 1.21 (t, J = 7.1 Hz, 3 H), 1.72 (s, 6 H), 3.77 (q, J = 7.1 Hz, 2 H), 4.55 (d, J = 6.7 Hz, 1 H), 5.91 (d, J = 6.7 Hz, 1 H); IR 1943 cm^{-1}.

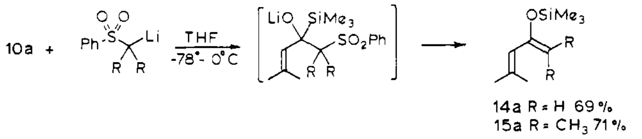
(7) For **8a**: MCPBA (1 equiv), pentane, -10 °C, 15 min; 25 °C, 45 min. For **8b**: MCPBA (1 equiv), CH_2Cl_2, −78 °C, 20 min; 0 °C, 45 min.

(8) The metalations were generally carried out with n-BuLi/THF, −78 °C, 30 min. Compound **9** (R_1 = CH_3, R_2 = H) was deprotonated with *sec*-BuLi/THF, −78 °C, 15 min. The derivatizations with Ph_2Se_2, Me_3SiCl, and CH_3I proceeded essentially exclusively at the γ-position.

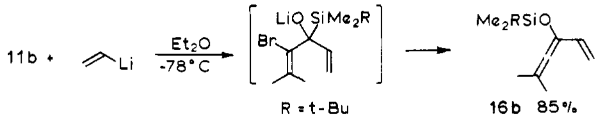
by [2,3]-sigmatropic rearrangement of an allenyl selenoxide.[3d] Introduction of the required organoseleno group was most effectively carried by the two-step procedure shown;[9] direct reaction of the allenyllithium with Ph_2Se_2 gave lower yields. Compound **13b** was prepared simlarly in 52% overall yield by methylation of **4b** followed by the selenation–oxidation sequence. Compounds **12b** and **13b**[6c] are canary-yellow liquids which, like the silyl enones discussed earlier, can be distilled and handled without special precautions,[10] although they are somewhat light sensitive and are best stored in the freezer.

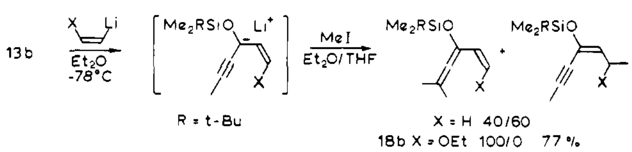


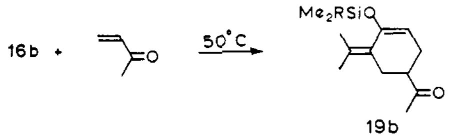
The availability of these new types of silyl ketones allows us to extend our synthetic applications of the Brook rearrangement.[1] Reaction of α-heterosubstituted lithium reagents with enone **10a** gives the siloxydienes **14a** and **15a**, the expected products of β elimination from the carbanion formed by [1,2] silicon rearrangement. The advantage of this approach to siloxydienes is its regiospecificity. The usual route involves enolization–silylation of enones, a reaction which cannot always be adequately controlled.



Unlike siloxydienes, siloxyvinylallenes, such as **16**, cannot be prepared by the enolization–silylation of carbonyl compounds.[11] In a reaction similar to the siloxydiene synthesis described above, addition of alkenyllithium reagents to α-halo silyl enones gives siloxyvinylallenes. We have also prepared compounds of this type by alkylation of pentaenynyl anions formed by addition of alkenyllithium reagents to α,β-acetylenic silyl ketones. The first method, illustrated by the preparation of **16b**, may be more general than the second, since success in the latter depends on the regioselectivity of an alkylation. Pentaenynyl anions are usually alkylated at one or both of the termini, depending on substitution.[12] This is illustrated in the two cases shown below. Reaction of vinyllithium with **13b** followed by [1,2]-silicon migration gives an anion (**17**, X = H) which is alkylated by methyl iodide to form two products. *cis*-2-Ethoxyvinyllithium,[13] on the other hand, gave only vinylallene **18b**.[6d] Furthermore, the cis stereochemistry of the lithium reagent was retained in the product.







We feel that siloxyvinylallenes may have some interesting uses as Diels–Alder dienes for the synthesis of alkylidenecyclohexanone derivatives (e.g., **19b**, the only regioisomer detected).[14] Work on the chemistry of the various polyfunctional compounds described here is continuing.

Acknowledgment. We thank the National Science Foundation and the Wisconsin Alumni Research Foundation for support of this research.

---

(9) Brandsma, L.; Wijers, H.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1962**, *81*, 583. Liotta, D.; Zima, G.; Barnum, C.; Saindane, M. *Tetrahedron Lett* **1980**, 3643. Mikolajczyk, M.; Grzejszczak, S.; Korbacz, K. *Ibid.* **1981**, 3097.

(10) We routinely add a small amount of radical inhibitor (3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide) to these materials to prevent polymerization.

(11) Siloxyallenes with a different substitution pattern have been prepared by reaction of 2-furyllithium with silyl ketones,[2b] and reaction of silylynamines with ketene (Henn, L.; Himbert, G. *Chem. Ber.* **1981**, *114*, 1015).

(12) Bertrand, M.; Dulcere, J. P.; Gil, G.; Roumestant, M. L. *Tetrahedron Lett.* **1979**, 1845. Delbecq, F.; Baudovy, R.; Gore, J. *Nouv. J. Chim.* **1979**, *3*, 321. Baudouy, R. Delbecq, F.; Gore, J. *J. Organomet. Chem.* **1979**, *177*, 39. Masamune, T.; Murase, H.; Matsue, H.; Murai, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 135. Dulcere, J.-P.; Grimaldi, J.; Santelli, M. *Tetrahedron Lett.* **1981**, *22*, 3179.

(13) Wollenberg, R. H.; Albizati, K. F.; Peries, R. *J. Am. Chem. Soc.* **1977**, *99*, 7365. Ficini, J.; Falou, S.; Touzin, A.-M.; d'Angelo, J. *Tetrahedron Lett.* **1977**, 3589. Lau, K. S. Y.; Schlosser, M. *J. Org. Chem.* **1978**, *43*, 1595.

(14) Vinylallene [2 + 4] cycloadditions have been only infrequently studied: Jones, E. R. H.; Lee, H. H.; Whiting, M. C. *J. Chem. Soc.* **1960**, 341. Fedorova, A. V.; Petrov, A. A. *Zh. Obschc. Khim.* **1962**, *32*, 3537. Bertrand, M.; Grimaldi, J.; Waegell, B. *Bull. Soc. Chim. Fr.* **1971**, 962. Heldeweg, R. F.; Hogeveen, H. *J. Org. Chem.* **1978**, *43*, 1916.

Pentadienyl Compounds of Vanadium, Chromium, and Manganese

David R. Wilson,[1] Ju-Zheng Liu, and Richard D. Ernst*

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received July 8, 1981

We recently reported the synthesis and characterization of several methylated bis(pentadienyl)iron complexes for which the general classification of "open ferrocenes" was shown appropriate.[2] These reddish compounds mimicked their ferrocene analogues in many regards such as solubility, volatility, air stability, and their general structural natures as demonstrated by ^1H NMR spectroscopy and an X-ray diffraction study of bis(2,4-dimethylpentadienyl)iron. Several considerations have indicated to us that a relatively large class of stable pentadienyl compounds ought to exist. The first, as previously described,[2] is that the π molecular orbitals of a pentadienyl ligand[3] in a "u" conformation are analogous in symmetry, orientation, and nodal properties to those of the closed cyclopentadienyl ligand. Further, the energies of the potential donor and acceptor orbitals of the pentadienyl ligand are, respectively, higher and lower than those of the cyclopentadienyl system,[3] suggesting the possibility of even stronger metal–ligand interactions. These first observations, however, do not take into account the cyclic nature of the cyclopentadienyl ligand, which likely imparts further kinetic stabilization nor do they take into account the larger size of the pentadienyl ligands, which may cost some orbital overlap. Here, however, one can make a comparison between alkyl, allyl, and pentadienyl ligands. The fact that allyl compounds generally tend to be more stable than alkyl compounds would suggest that (at least pentahapto bound) pentadienyl compounds should be even more stable, essentially through chelation and delocalization influences.[4] Indeed, these considerations seem to be borne out by subsequent theoretical calculations and Mössbauer data.[5] In order to test the validity

---

(1) NSF Predoctoral Fellow, 1980–present.

(2) Wilson, D. R.; DiLullo, A. A.; Ernst, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5928.

(3) Streitwieser, A., Jr. "Molecular Orbital Theory for Organic Chemists"; Wiley: New York, 1961.

(4) Wilke, G.; Bodgdanovic, B.; Hardt, P.; Heimbach, P.; Keim, W.; Kroner, M.; Oberkirch, W.; Tanaka, K.; Steinrucke, E.; Walter, D.; Zimmermann, H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 151.

0002-7863/82/1504-1120$01.25/0