

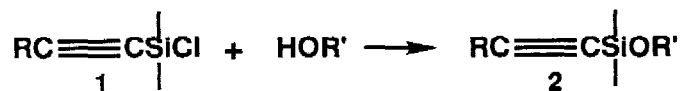
AN EFFICIENT SYNTHESIS OF ALKENYL AND ALKYNYL SILYL ETHERS

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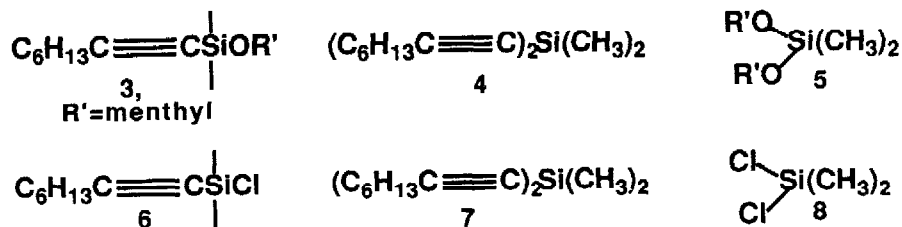
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Summary: A general synthesis of alkynyl and alkenyl silyl ethers is described. This involves reaction of alkynyl or alkenyl organometallic reagents, usually the lithio derivatives, with chlorodimethylaminodimethylsilane, followed by reaction of the product with an alcohol.

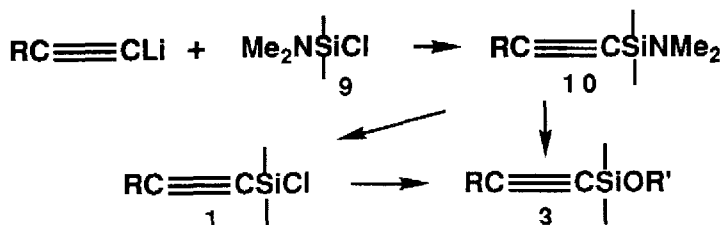
Our interest in the chemistry of alkynyl and alkenyl silyl ethers made us realize the inadequacy of the available routes to alkenyl and alkynyl chlorosilanes,¹ the obvious intermediates (cf 1 → 2) to the desired ethers. The problem arises from the lack of specificity in



the reaction of dimethyl dichlorosilane with alkenyl or alkynyl organometallic reagents:² we found, for example, that slow addition of a THF solution of octynyl lithium to 1 equiv of dichlorodimethylsilane (THF, -78 °C, 30 min; room temperature, 1 h), followed by ether formation with menthol produced a mixture of 3, 4 and 5 (capillary GC analysis and comparison with authentic samples) which corresponded to an initial mixture of 6, 7 and 8 in the ratio of 1.0: 2.1: 2.5. A more selective method was clearly required.



We now report a generally useful solution to this problem. This starts with the reaction of an alkynyl lithium with dimethylaminodimethylchlorosilane (**9**),³ as shown in the Scheme:



Scheme

The same procedure can be used starting with a lithium alkenyl.^{4,5} The silylamines **10** thus obtained can themselves normally be used to make the required silyl ethers.⁶ Reaction of 1 equiv of **10**, R=C₆H₁₃, with 1 equiv of menthol gave the alkynyl silyl ether **3** in 97% yield. Alkenyl and allyl silyl ethers were easily made in the same manner. The table next page shows the overall yields of silyl ethers obtained from the relatively base-sensitive 2-bromocyclohexanol by this method.

In certain cases, the dimethylamine liberated in the ether formation step **10**→**3** may result in an unwanted reaction, such as conjugate addition. The use of a chlorosilane would be more satisfactory in such a situation, and it is, therefore, very useful that elusive chlorosilanes such as **1** can be made easily from the aminosilanes **10** by treatment with anhydrous hydrogen chloride.^{4b}

General Procedure for Preparing Silylacetylenic Ethers: A solution of the terminal acetylene in dry THF (~1.8M) is cooled to -78 °C. One equiv of n BuLi in hexane is then added, followed, after ten minutes, by one equiv of freshly distilled N,N-dimethylaminodimethylchlorosilane. After ten minutes, the reaction is warmed to room temperature, 1.05 equiv of the desired alcohol is added and the reaction mixture is stirred overnight (3-4 h is often sufficient). The solvent is removed under reduced pressure and the crude mixture is filtered through a short pad of Florisil, usually in an ether/hexane mixture. Removal of the solvent under reduced pressure gives the silylacetylenic ether which is normally pure enough for further reactions.

Anion precursor	Product	Yield (%) ^a
		85
b		60
b		87
b, c		47
b		90
b		98

a. Except for the acetylenes, the yields have not been maximized.
 b. Metallated with *n*-BuLi in THF at -78°C.
 c. 4:1 mixture of *Z* and *E* isomers.

Acknowledgments: We thank the National Institutes of Health and the National Science Foundation for their support of this work.

References and Notes

- 1) Chlorodimethyl vinylsilane seems to be the only readily available member of this group. It is available commercially.
- 2) (a) H. Matsumoto, T. Kato, I. Matsubar, Y. Oshino, Y. Nagai *Chem. Lett.*, **1979**, 1287. (b) N.V. Komarov, L.I. Ol'khovskaya, K.S. Pushkareva, L.A. Soboleva, *Zh. Obshch. Khim.*, **1984**, *54*, 1584. (c) O.N. Florenzova, B.A. Sokolov, L.I. Volkava, *Izv. Akad. Nauk SSR, Ser. Khim.*, **1973**, 1390.
- 3) This can be prepared easily: cf S.S. Washburn and W.R. Peterson, *J. Organomet. Chem.*, **1970**, *21*, 59. It is also available commercially from Huls America, Piscataway, New Jersey.
- 4) (a) A reaction of **9** with a phenyl grignard reagent has been mentioned: B.N. Ghose, *J. Organometal Chem.*, **1979**, *164*, 11; (b) G. Chandra, W.J. Owen, N.C. Lloyd and B.E. Cooper; U.S. Patent 3,714,118; *Chem. Abstracts*, **1973**, *78*, 137285.
- 5) Note that the reaction is an addition-elimination process and not a direct displacement (bond dissociation energies: Si-N, 76 kcal/mol; Si-Cl, 127 kcal/mol. See E.A.V. Ebsworth in "Organometallic Compounds of the Group IV Elements," A.G. McDiarmid, ed.; Marcel Dekker, New York, 1968, vol.1, part 1, chapter 1).
- 6) Compare I. Weisz, K. Felfoldi and K. Kovacs *Acta Chim. Hung.*, **1968**, *58*, 189
- 7) The aminosilane was distilled before use, after refluxing under argon with quinoline or over calcium hydride for 2-3 h.

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