Tetrahedron Letters,Vol.28,No.5,pp 511-514,1987
Printed in Great Britain

0040-4039/87 $3.00 + .00
Pergamon Journals Ltd.

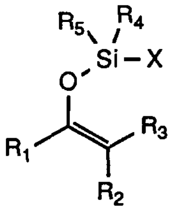
SILICON-FUNCTIONALIZED SILYL ENOL ETHERS: A NOVEL DIALKYLCHLOROSILYL ENOL ETHER AND ITS CONVERSION TO ALKOXY- AND AMINOSILYL ENOL ETHERS

Robert D. Walkup

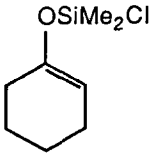
Department of Chemistry and Biochemistry
Texas Tech University
Lubbock, TX 79409-4260

Abstract: The lithium enolate derived from 3,3-dimethyl-2-butanone (pinacolone) reacted with dichlorodimethylsilane to yield a chlorosilyl enol ether, 3,3-dimethyl-2-(chlorodimethylsilyloxy)-1-butene, which reacts with numerous oxygen and nitrogen nucleophiles to yield silicon-functionalized silyl enol ethers.

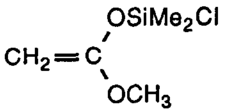
Trialkylsilyl enol ethers (trialkylsilyloxyalkenes) and related silyl ketene acetals have enjoyed widespread usage in organic syntheses.[1] However, little attention has been paid to the effect that varying the silicon-bound ligands has upon the reactivity of silyl enol ethers in such reactions as Lewis acid-mediated aldol additions,[2] oxidations to form α-hydroxycarbonyls,[3] [3,3]-sigmatropic rearrangements,[4] and [4+2]-cycloadditions[5] which involve these enol derivatives; in all of the reported cases of these reactions, simple alkyl groups are employed on the silicon atom, and are considered to exert little or no effect upon the reaction. We envision that a judiciously chosen non-alkyl ligand (X in **1**) placed on the silicon in a silyl enol ether **1** may profoundly affect the reactivity of such enol ethers by altering the electron distribution in the enol ligand or by introducing a new functional group "handle" which may have a directing effect (e.g., via chelation or dipole-dipole interactions) upon a reagent engaging with the enol ether. With this vision in mind, we consider a chlorosilyl enol ether (**1**: X = Cl) to be an appropriate example of such a silicon-functionalized silyl enol ether, and it can also function as a precursor for a variety



1



2



3

of other Si-functionalized enol ethers because of the susceptibility of the Si-Cl bond to nucleophilic substitution[6].

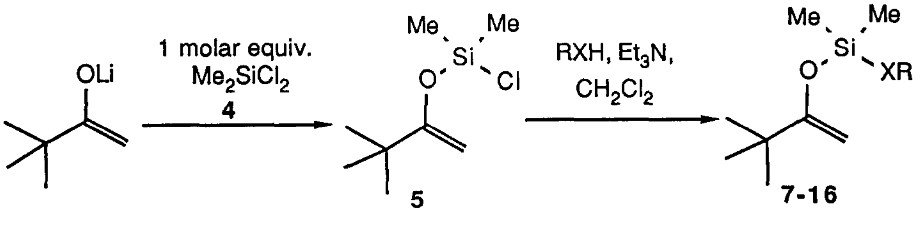
To date one chlorosilyl enol ether, the cyclohexene 2, and one chlorosilyl ketene acetal, 3, have been reported. The ether **2** was synthesized from cyclohexanone and dichlorodimethylsilane (**4**) in the presence of triethylamine and zinc chloride,[7] and **3** was formed by heating methyl tripropylstannylacetate with **4**.[8]

It occurred to us that chlorosilyl enol ethers could be formed by the reaction of a lithium enolate with a dialkyldichlorosilane such as **4**, provided that a second substitution reaction (to form a bis(alkenyloxy)silane)[9] would not occur. We report here the first synthesis of a chlorosilyl enol ether (**5**) from a lithium enolate, and describe some transformations of this enol ether which suggest that such chlorosilyl enol ethers will indeed be pinguid precursors for a number of synthetically useful silyl enol ethers.

When the lithium enolate derived from 3,3-dimethyl-2-butanone (pinacolone) is allowed to react with 1 molar equivalent of **4**, the enol ether **5** is formed in good yield and bears no trace of the bis-adduct **6** (Scheme).[10] The bis-adduct **6** can be formed, however, when 0.5 molar equivalent of **4** is allowed to react with the lithium enolate (Table).[11] The chlorosilyl enol ether **5** evolves acidic fumes and slowly forms a white polymeric precipitate upon standing. The structure of this precipitate is not yet known to us, but its formation does not affect the integrity of the clear supernatant, which assays by ^{1}H-NMR to be pure **5** even after several months of storage at 0°C.

As expected, the chlorosilyl enol ether **5** readily reacts with protic nucleophiles to form Si-functionalized silyl enol ethers such as **7-16** (Scheme and Table).[12] The reaction of **5** with 0.5 molar equivalents of water yields **7**. Treatment of **5** with any of a number of alcohols yields the alkoxydialkylsilyl enol ethers **8-15** in good yields, and the reaction of **5** with diethylamine yields the dialkylaminosilyl enol ether **16**.[13]

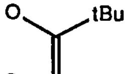
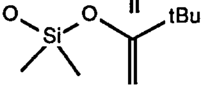
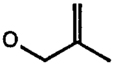
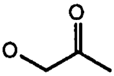
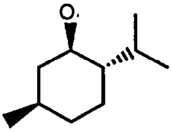
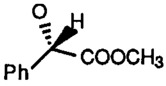
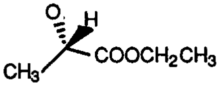
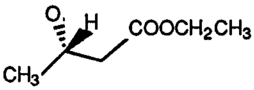
Scheme



Three alkoxydialkylsilyl enol ethers have been reported, one arising from a Pt-catalyzed hydrosilylation of an enone by ethoxydiethylsilane,[14] another by the treatment of a β-diketone with dicyanodimethylsilane,[15] and a third by the reaction of an enolizable ketone with bromo tert-butylmethoxyphenylsilane and triethylamine.[16] Dialkylaminosilyl enol ethers, to our knowledge, have not been reported up to now. Our synthesis of **16** suggests that aminosilyl enol ethers are readily accessible from chlorosilyl enol ethers and amines.

Investigations of the syntheses and properties of the many interesting classes of Si-functionalized silyl enol ethers which, based on the results discussed above, are readily available from chlorosilyl enol ethers such as **5** are continuing in our laboratory.[17].

Table. Silicon-Functionalized Silyl Enol Ethers from a Chlorosilyl Enol Ether.

Structure Number[a]	XR (See Scheme)	Yield (%)[b]	^{1}H-NMR (ppm)[c]	IR (NaCl) (cm^{-1})[d]
6		96	4.18(m,4H); 0.97(s,18H); 0.17(s,6H).	2980; 1625.
7		61	4.10(m,4H); 1.03(s,1BH); 0.17(s,12H).	2980; 1625.
8	OCH_2CH_3	79	4.09(br s,1H); 4.07(br s,1H); 3.74(q,2H,J=7); 1.17(t,3H,J=7Hz); 1.03(s,9H); 0.12(s,6H).	2950; 1625.
9		80	4.97(br s,1H); 4.80(br s,1H); 4.09(br s,4H); 1.73(br s, 3H); 1.10(s,9H); 0.23(s,6H).	2980; 1625.
10		66	4.30(s,2H); 4.13(d,2H,J=4 Hz); 4.10(d,2H,J=4 Hz); 2.20(s,3H);1.12(s,9H);0.27(s,6H).	2970; 1740; 1625.
11		89	4.53(t,1H,J=5 Hz); 4.12(s,2H); 3.73(d,2H,J=5 Hz); 3.70(t,2H,J=6 Hz); 3.67(t,2H,J=6 Hz); 1.57(t,6H, J=6 Hz); 1.12(s,9H); 0.23(s,6Hz).	2800; 1620.
12		88	4.03(d,1H,J=2Hz); 4.00(d,1H,J=2 Hz); 3.60 (m,1H); 1.4(br m,3H); 1.08(s,9H); 1.00(d,6H,J=6 Hz); 0.9(br m,6H); 0.83(d,3H,J=6 Hz); 0.20(s,6H).	2980; 1625.
13		48	7.40(m,5H); 5.47(s,1H); 4.10(m,2H); 3.70(s,3H); 1.13(s,9H); 0.27(s,3H); 0.17(s,3H).	3000; 1750; 1625; 1600; 1500.
14		31	4.50(q,1H,J=7 Hz); 4.20(q,2H,J=7 Hz); 4.13(s,2H); 1.40(t,3H,J=7 Hz); 1.12(s,9H); 1.05(d,3H,J=7Hz); 0.27(s,3H); 0.23(s,3H).	2980; 1752; 1625.
15		61	4.43(pent,1H,J=6 Hz); 4.13(q,2H,J=7 Hz); 4.11(d, 1H,J=1 Hz); 4.08(d,1H,J=1 Hz; 2.50(d,1H,J=6 Hz); 2.40(d,1H,J=6 Hz); 1.26 (d,3H,J=6 Hz); 1.23(t,3H,J=7 Hz); 1.10(s,9H);0.21(s,6H).	2980; 1740; 1625.
16	$N(CH_2CH_3)_2$	68	4.03(d,1H,J=1 Hz); 3.93(d,1H,J=1 Hz); 2.88(q,4H, J=6 Hz); 1.10(s,9H); 1.02(t,6H,J=6 Hz); 0.20(s,6H).	2980; 1625.

---

[a] All of these compounds exhibited analytical and/or mass spectral behavior commensurate with high purity and identity.

[b] Yields are of products after purification by chromatography or distillation.

[c] Measured using a Varian EM-360 spectrometer ($CDCl_3$, TMS standard).

[d] Measured using a Nicolet MX-S spectrophotometer (film, NaCl plates).

References

1) Brownbridge, P. Synthesis 1983, 1; 85; Rasmussen, J. K. Synthesis 1977, 91.

2) Mukaiyama, T. Angew. Chem. Int. Ed. 1977 16, 817.

3) Rubottom, G. M., Vazquez, M. A.; Pelegrina, D. R. Tetrahedron Lett. 1974, 4319.

4) Ireland, R. E., Mueller, R. H., Willard, A. K. J. Am. Chem. Soc. 1976, 98, 2868.

5) Danishefsky, S. Acc. Chem. Res. 1981, 14, 400; see also Petrzilka, M., Grayson, J. I. Synthesis 1981, 753.

6) Fleming, I. in: Comprehensive Organic Chemistry, Barton, D. H. R. and Ollis, W. D., eds., volume 2, 1979, chapter 13.

7) French Patent 2,253,751 (1975), Societe des Usines Chimiques Rhone-Poulenc (Chem. Abstracts 1976, 84, 58761z).

8) Lutsenko, I. F., Baukov, Yu. I., Burlachenko, G. S., Khasapov, B. N. J. Organometal. Chem. 1966, 5, 20.

9) Fataftah, Z. A., Ibrahim, M. R., Abu-Agil, M. S. Tetrahedron Lett. 1986, 27, 4067.

10) Dry diisopropylamine (4.5 ml, 32.1 mmol) is stirred under argon in 75 ml dry diethyl ether at -78°C while a 2.3 M hexane solution of n-butyllithium (14.0 ml, 32.2 mmol) is added dropwise. A solution of pinacolone (3.006 g, 30.0 mmol) in 15 ml diethyl ether is added dropwise after 15 minutes, then the solution is stirred for another 30 minutes. Dichlorodimethylsilane (3.7 ml, 30.5 mmol) is then added, and the solution is then allowed to warm to room temperature over 5 hours. The resulting suspension is then concentrated to a volume of 20 ml, filtered through celite, then distilled under vacuum to yield 4.0 g (70%) of a clear, colorless liquid, bp 27-30° (2.1 mm Hg). ^{1}H-NMR (CDCl$_3$/TMS): $\delta = 4.30$ (s,2H); 1.10 (s,9H); 0.55 (s,6H). IR (NaCl): $\nu = 2980, 1627$ cm^{-1}. (Due to the reactivity of this compound, a satisfactory elemental analysis could not be obtained).

11) This synthesis of a bis(alkenyloxy)silane closely resembles a recently-reported synthetic route to this class of Si-functionalized silyl enol ethers (ref. 9). In addition, bis(3-phenyl-1-propen-1-yloxy)phenylsilane has been reported as the product from a Rh-catalyzed hydrosilylation of cinnamaldehyde: Ojima, I., Kogure, T., Nihonyanagi, M., Nagai, Y. Bull. Chem. Soc. Japan 1972, 45, 3506.

12) General Procedure for the synthesis of enol ethers 7-16: To a solution of 10 mmol of 5 (formed in situ, thus a solution in ether containing diisopropylamine, hexane and LiCl) at 0°C is added 1.5 ml (10.8 mmol) triethylamine followed by 10 mmol of an alcohol or amine (5 mmol of H_2O to form 7). The mixture is then stirred at 25°C overnight. A standard aqueous workup/drying protocol followed by flash chromatography (silica gel, 95:5 hexane:ethyl acetate) or distillation yields pure 7-16 (Table).

13) B.p. 101-105° C (2.5 mm Hg). This compound decomposed on silica gel when purification by chromatography was attempted.

14) Yoshii, E., Ikeshima, H., Ozaki, K. Chem. Pharm. Bull. 1972, 20, 1827.

15) Ryn, I., Murai, S., Shinonoga, A., Horiike, T., Sonoda, N. J. Org. Chem. 1978, 43, 780.

16) Guindon, Y., Fortin, R., Yoakim, C., Gillard, J. W. Tetrahedron Lett. 1984, 25, 4717.

17) This research was made possible by the financial assistance of the Robert A. Welch Foundation and the Donors of the Petroleum Research Fund of the American Chemical Society.

(Received in USA 22 September 1986)