CHEMISTRY LETTERS, pp. 1055-1058, 1990.

Effects of Variations of Alkoxy Substituents upon Cyclizations of Dialkoxy-2-chloroethylsilyl Enol Ethers to form 2,2-Dialkoxy-1-oxa-2-silacyclohexanes[1)]

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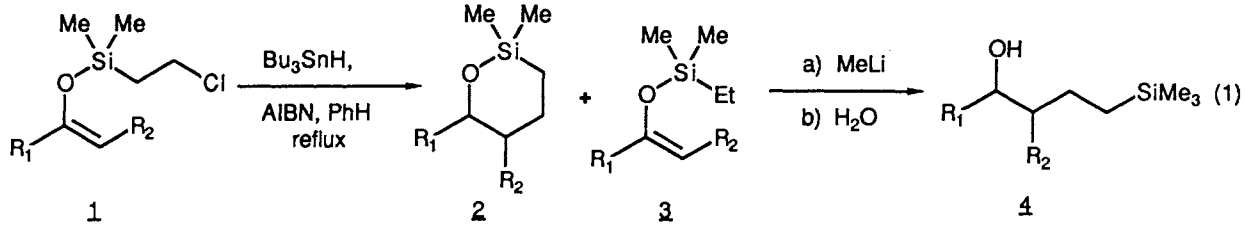
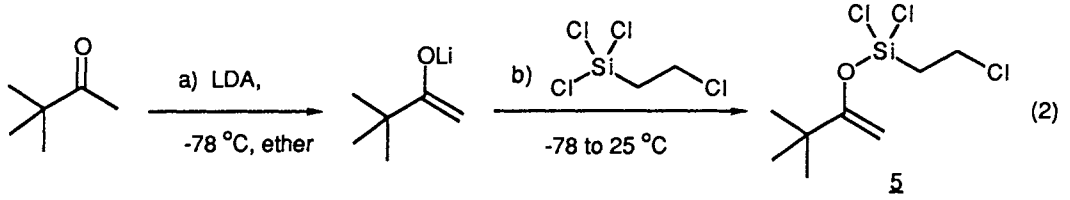
Various dialkoxychloroethylsilyl enol ether derivatives of pinacolone, upon treatment with tributylstannane and AIBN, underwent free-radical cyclizations to yield isolable 2,2-dialkoxy-1-oxa-2-silacyclohexanes. As the bulkiness of the alkoxy groups increased, the selectivity of the reaction for forming cyclized instead of directly reduced acyclic byproducts improved.

We recently reported the cyclizations of various chloroethyldimethylsilyl enol ether derivatives of ketones (1) with tributlystannane by a free-radical process to yield mixtures of 1-oxa-2-silacyclohexanes (2) and ethyldimethylsilyl enol ethers (3), as shown in equation 1.[2)] Due to the instability of the oxasilycyclohexanes and difficulties in removing alkyltin byproducts, the crude mixtures of 2 and 3 were treated with methyllithium to yield, upon workup, isolable trimethylsilyl alcohols 4 (Eq. 1).[2)] This synthetically useful "reductive alkylation" of ketones has the disadvantage that significant amounts of uncyclized reduction product 3 were formed. Therefore, we decided to study the effects of replacing the methyl substituents on the silicon atom in 1 by alkoxy groups upon the cyclization reaction.



1 2 3 4

For ease of handling and analysis, we used the enolate of pinacolone for this study. The lithium enolate was formed by stirring the ketone with LDA at -78 °C in ether for 10 min. Chloroethyltrichlorosilane (1 molar equiv.) was then added, and the mixture was allowed to warm to room temperature.[3)] Filtration through celite followed by distillation yielded the chloroethyldichloro-silyl enol ether 5 as a colorless fuming liquid in 36% yield (Eq. 2).[4)] Compound 5 is the first dichlorosilyl

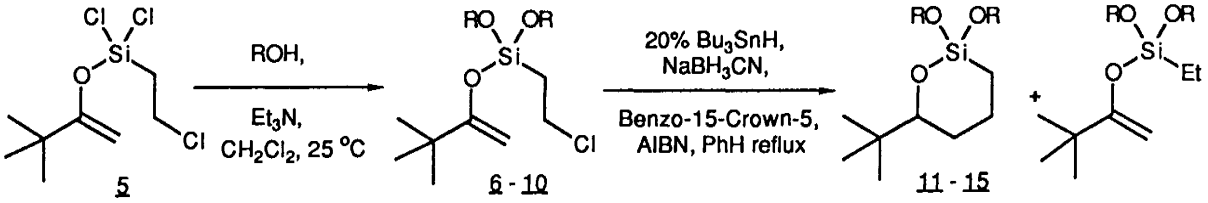


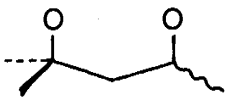
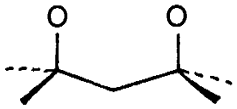
5

enol ether to be reported.[3] When 5 was stirred overnight, at 25 °C in dichloromethane and triethylamine (2 molar equiv.) with a monoalcohol (2 equiv.) or a diol (1 equiv.), dialkoxychloroethylsilyl enol ethers were formed in good yields. In this manner, the five dialkoxysilyl enol ethers 6-10 indicated in Table 1 were prepared. The low yield obtained for the enol ether 10 was attributed to the sluggishness of the reaction between the bulky diol 2,4-dimethyl-2,4-pentanediol and the bulky dichlorosilane 5. The structures of each of the dialkoxysilyl enol ethers was clearly indicated by their ^{1}H- and ^{13}C-NMR and IR spectra.[5]

When the chloroethylsilyl enol ethers 6-10 were subjected to the free-radical cyclization conditions,[2,6] mixtures of the 2,2-dialkoxy-1-oxa-2-silacyclohexanes 11-15 and the corresponding uncyclized byproducts (dialkoxyethylsilyl enol ethers) were formed. The ratios of the cyclized to uncyclized products present in the crude reaction mixtures were determined by ^{1}H-NMR spectroscopy[7] with the results indicated in Table 1. The 2,2-dialkoxy-1-oxa-2-silacyclohexanes 11-15 were then isolated from the product mixtures by chromatography, and their structures were verified by NMR analysis.[8]

Table 1. Syntheses and Cyclizations of Dialkoxychloroethylsilyl Enol Ethers



Entry	RO	Dialkoxy-silyl enol ether	Yield of enol ether	Ratio of cyclized (11-15) to uncyclized product[e]	Oxasila-cyclo-hexane	Isolated yield of oxasila-cyclohexane[c]
1	CH_3O	6	68%[a]	75:25	11	30%
2	CH_3CH_2O	7	76%[b]	80:20	12	35%
3		8	83%[c]	75:25	13	40%
4		9	88%[c], [d]	85:15	14	31%
5		10	21%[c]	90:10	15	30%

a) Distilled (bp 70-72 °C. (1 mmHg)). b) Obtained in >95% purity after workup; not purified any further. c) Purified by chromatography on 230-400 mesh silica gel using a 95:5 hexane:ethyl acetate eluent. d) Formed as a 70:30 mixture of diastereomers epimeric at the silicon center. e) See Ref. 7.

The results of this study reveal four notable facts concerning silicon-functionalized silyl enol ethers and the free-radical cyclizations of chloroethylsilyl enol ethers. First, our results imply that dialkoxysilyl enol ethers like 6-10 can be readily synthesized and isolated when the enoxy substituent is a bulky one such as the pinacolone-derived enolate; preliminary results indicate that dialkoxysilyl enol ether derivatives of less bulky ketones can be obtained, but they are highly susceptible to hydrolytic decomposition during handling. Second, we have observed that the tractability of dialkoxysilyl enol ethers like 6-10 is improved as the bulkiness of the alkoxy groups is increased, as judged by the increasing yields of isolated enol ethers observed in the series going from 6 (RO = CH_3O) to 9 (RO = 2-methyl-2,4-pentanedioxy). However, this trend is limited by the apparent inability of a very bulky alcohol to react with the chlorosilyl enol ether (cf. 10, Table 1).

A third fact to emerge from our study is that the ratios of cyclized to uncyclized products from the free-radical reaction increased as the bulkiness of the alkoxy groups present on the silicon atom increased. We speculate that this trend is due to the two bulky alkoxy groups repelling one another, thus increasing the RO-Si-OR bond angle and causing a commensurate decrease in the enoxyO-Si-CH_2CH_2• bond angle in such a way that the approach of the β-silylethyl radical to the enoxy C=C bond is enhanced. Confirmation of such an idea must await further experimentation.[9]

A fourth fact revealed by our experimental results is that 2,2-dialkoxy-1-oxa-2-silacyclohexanes like 11-15 are stable enough to aqueous workup and chromatography to be isolated in pure form, unlike the 2,2-dimethyl-1-oxa-2-silacyclohexanes which we previously reported.[2]

Oxasilacyclohexanes are monomers for interesting polymeric materials.[10] Our synthetic approach to these heterocycles, which starts with ubiquitous carbonyl compounds as enoxy precursors, is unique[11] and capable of producing polyfunctionalized and/or chiral oxasilacyclohexane monomers which could be used to produce silicon-containing polymers having unique properties, as well as useful organosilicon intermediates for organic synthesis.

This research was made possible by a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society (grant #19870-AC1). The NMR spectrometer employed was purchased using funds provided by the National Science Foundation (#CHE-8511404).

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2) R.D. Walkup, R.R. Kane,and N.U. Obeyesekere, Tetrahedron Lett., 31, 1531 (1990).

3) For a discussion of the syntheses of monochlorosilyl enol ethers, see R.D. Walkup, Tetrahedron Lett., 28, 511 (1987).

4) Bp 52-54 °C (1 mmHg). ^{1}H-HMR ($CDCl_3$, TMS standard): δ 4.43 (1H, d, J=2.5 Hz), 4.39 (1H, d, J=2.5 Hz), 3.72-3.82 (2H, ABXY multiplet), 1.83-1.91 (2H, ABXY multiplet), 1.08 (9H, s).

5) Diagnostic ^{1}H-NMR signals for 6-10: 2H singlet (6,8) or two 1H doublets (J=1-2 Hz) (7, 9, 10) at 4.1-4.4 ppm; 9H singlet at 1.0-1.1 ppm and typical signals for the dialkoxy moiety, with the correct integrations relative to those for the enoxy group. Diagnostic ^{13}C-NMR signals for 6-10: 165.0-165.2 ppm and 87.5-88.7 ppm for alkene carbons, and typical signals for the dialkoxy moiety. Diagnostic IR absorption for 6-10: 1626-1630 cm^{-1}.

6) A "catalytic tin" recipe, similar to that of G. Stork and P.M. Sher, J. Am. Chem. Soc., 108, 303

(1986), was used for this study: a 0.02 M solution of the enol ether plus 3 molar equiv. of sodium cyanoborohydride, 0.1 molar equiv. of benzo-15-crown-5, and 0.2 molar equiv. of tributylstannane in dry deoxygenated benzend were brought to reflux under nitrogen, then a 0.1 M solution of 0.3 molar equiv. of AIBN, in dry benzene, was added over the course of 4-6 h. The mixture was allowed to reflux for an additional 6 h, then cooled, filtered through celite, then concentrated. The crude reaction mixture was submitted to ^{1}H-NMR analysis (Ref. 7), then to chromatography on silica gel (in the cases of 11 and 12, on florisil) to yield the pure 2,2-dialkoxy-1-oxa-2-silacyclohexanes in the yields indicated in Table 1.

7) Observed, in each case: disappearance of the ABXY signal at 3.7 ppm (CH_2Cl for chloroethylsilyl group); disappearance of the signals at 4.4 ppm ($C=CH_2$ of starting silyl enol ether); appearance of a new multiplet at ≈0.55 ppm (CH_2 next to Si in the oxasilacyclohexane); appearance of a new multiplet at ≈3.6 ppm (CH-O in the oxasilacyclohexane); appearance of a new broad singlet at ≈3.9 ppm [always ≈0.1-0.2 ppm upfield from the $C=CH_2$ signals of the starting silyl enol ether] ($C=CH_2$ of the ethyldimethylsilyl enol ether byproduct). Relative integrations of the signals for the CH-O (cyclized) vs. the $C=CH_2$ (uncyclized) hydrogens allowed the ratio of cyclized to uncyclized products to be estimated.

8) Diagnostic ^{1}H-NMR signals for 11-15: 1H doublet of doublets (J=2, 7 Hz) at 3.56-3.62 ppm; 9H singlet at 0.87-0.89 ppm; 2H ABXY multiplet at 0.5-0.6 ppm and typical signals for the dialkoxy moiety, with the correct integrations relative to those for the oxasilacyclohexane moiety. Diagnostic ^{13}C-NMR signals for 11-15: 84.1-84.4 ppm for C_6 of the 1-oxa-2-silacyclohexane moiety and typical signals for the dialkoxy moiety.

9) For a discussion of some stereoelectronic effects of a β-silicon atom upon radical cyclizations of silahexenes, see J.W. Wilt, Tetrahedron, 41, 3979 (1985); J.W. Wilt, J. Lusztyk, M. Peeran,and K.U. Ingold, J. Am. Chem. Soc., 110, 281 (1988).

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(Received March 12, 1990)