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THE MOLECULAR STRUCTURE OF AN O-SILYL KETENE ACETAL [1]

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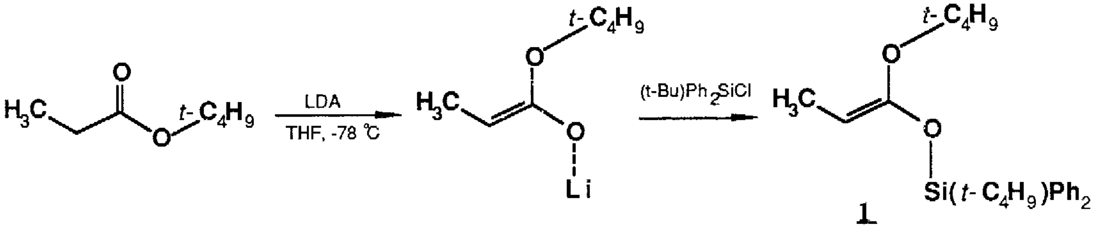
Abstract. The structure of E-[[1-(1,1-dimethylethoxy)-1-propenyl]oxy](1,1-dimethylethyl)diphenyl silane (1), as determined by single crystal x-ray diffraction analysis, is described.

Silyl ketene acetals are usually prepared from ester enolates and are important intermediates in many synthetic processes. Ireland *et al.* demonstrated that lithium ester enolates are obtainable as distinct geometrical isomers and deduced the identity of these isomers by analysis of the configurations of the Claisen rearrangement products obtained from rearrangement of the enolates from 2-butenyl propanoates.[3] The validity of Ireland's assignment was confirmed by Seebach *et al.* through direct crystal structure analysis of lithium ester enolates.[4] Silylation of enolate anions is reasonably believed to proceed without isomerization of the double bond geometry. The results described here furnish formal confirmation of this point and also provide the first structural details for a propanoate silyl ketene acetal.

The silyl ketene acetal (1) was prepared by the methods developed by the Ireland group.[3] Deprotonation of t-butyl propanoate was carried out by LDA in THF at -78 °C and the resulting enolate was silylated by t-butyl(diphenyl)silyl chloride. The acetal was isolated by diluting the reaction mixture with pentane and washing the organic material with 0.01 N NaOH and brine. After drying ($MgSO_4$) removal of volatile materials under reduced pressure afforded the ketene acetal which solidified at 0 °C and was recrystallized from n-hexane at -20 °C. The crystalline ketene acetal melted at 41 °C and was stable at room temperature.



The crystal structure for acetal **1** was determined by direct methods from data acquired at 163 °K.[5] The space group is triclinic [a=11.4124(29) Å, b=13.7280(26) Å, c=15.4659(36) Å; α=102.656(17), β=106.369(19), γ=100.833(18); V=2186.2(9) Å^3]. Two nearly identical but crystallographically unique molecules were located. Atomic coordinates for both molecules of **1** are given in Table 1. The atomic numbering adopted here is provided in Figure 1. A stereo view of one molecule is presented in Figure 2.

Figure 1.

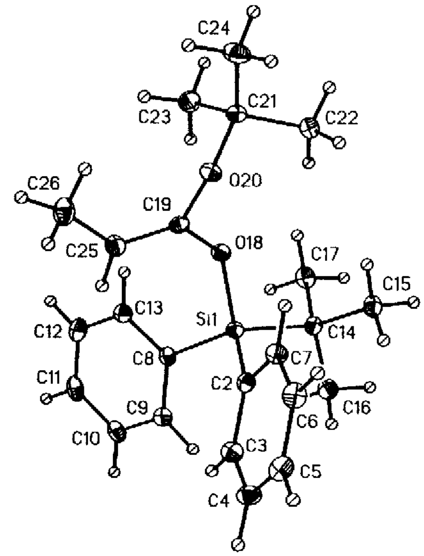


Table 1. Fractional Coordinates for non-H Atoms of Acetal **1**.

Atom	x	y	z	Atom	x	y	z
Si1	-.13018(4)	.14483(4)	.24952(4)	Si1'	.63119(5)	.41008(4)	.81783(4)
C2	-.1861(2)	.07356(13)	.12160(12)	C2'	.6769(2)	.36281(14)	.71253(13)
C3	-.3101(2)	.01299(15)	.07067(14)	C3'	.7798(2)	.4147(2)	.69393(15)
C4	-.3505(2)	-.0293(2)	-.02616(14)	C4'	.8097(2)	.3724(2)	.6152(2)
C5	-.2671(2)	-.0132(2)	-.07465(15)	C5'	.7382(2)	.2773(2)	.55414(15)
C6	-.1436(2)	.0443(2)	-.02612(14)	C6'	.6346(2)	.2250(2)	.57004(15)
C7	-.1037(2)	.08754(15)	.07050(14)	C7'	.6042(2)	.2673(2)	.64813(14)
C8	-.2104(2)	.07890(13)	.31945(12)	C8'	.7016(2)	.55123(14)	.87994(12)
C9	-.3426(2)	.04768(15)	.29644(14)	C9'	.8320(2)	.5994(2)	.91486(14)
C10	-.3980(2)	.00282(15)	.35218(15)	C10'	.8791(2)	.7030(2)	.96693(15)
C11	-.3231(2)	-.0120(2)	.4325(2)	C11'	.7985(2)	.7611(2)	.9856(2)
C12	-.1928(2)	.0192(2)	.45847(15)	C12'	.6690(2)	.7151(2)	.9518(2)
C13	-.1377(2)	.06355(14)	.40207(13)	C13'	.6220(2)	.6122(2)	.90027(14)
C14	-.1469(2)	.28127(14)	.26682(12)	C14'	.6688(2)	.3338(2)	.90463(13)
C15	-.0867(2)	.3329(2)	.2055(2)	C15'	.6030(3)	.2183(2)	.8595(2)
C16	-.2875(2)	.2799(2)	.2377(2)	C16'	.8122(2)	.3472(3)	.9415(2)
C17	-.0802(2)	.3442(2)	.37047(15)	C17'	.6248(2)	.3747(2)	.9873(2)
O18	.02483(11)	.16047(9)	.29294(9)	O18'	.47449(11)	.38657(10)	.78218(9)
C19	.0969(2)	.09246(14)	.27856(12)	C19'	.3964(2)	.39797(14)	.70152(12)
O20	.20411(11)	.13631(9)	.26439(8)	O20'	.29169(11)	.31669(9)	.65743(9)
C21	.2977(2)	.22767(14)	.33724(13)	C21'	.1984(2)	.29737(15)	.70506(14)
C22	.2646(2)	.3257(2)	.3211(2)	C22'	.2383(2)	.2341(2)	.7712(2)
C23	.3044(2)	.2196(2)	.43446(15)	C23'	.1805(3)	.3988(2)	.7533(2)
C24	.4206(2)	.2222(2)	.3192(2)	C24'	.0795(2)	.2333(2)	.6233(2)
C25	.0653(2)	-.00619(15)	.27471(14)	C25'	.4212(2)	.4750(2)	.66611(13)
C26	.1462(2)	-.0787(2)	.2631(2)	C26'	.3359(2)	.4891(2)	.5793(2)

The structure confirms that deprotonation of a propanoate ester in THF with LDA and trapping of the enolate with a silyl chloride affords the *E*-isomer of the ketene acetal. Seebach has already confirmed Ireland's configurational assignment for the enolate intermediate.[3,4] Therefore the present structure establishes directly that the silylation of enolates proceeds with retention of alkene geometry.

There are few structures known for 1,1-disubstituted alkenes in which both substituents are oxygen or nitrogen. The structures for some related molecules are presented in Figure 3. The double bond of **1** is short but not unusual for an electron rich alkene. It is similar in length to that reported for one enol ether and matches well the double bond length determined for ketene acetal **2**.[6,7] The double bond is significantly longer than that observed in the corresponding enolate **3**.[4] The C-O bond to the silyloxy oxygen atom is similar to that observed in silyl enol ether **4**.[8] The C-O bond from the alkene to the t-butoxy group is shorter than the corresponding bond to the silyloxy group (1.356 vs. 1.378 Å). This difference may be primarily due to an effect of the silicon. The interesting possibility that an anomeric

Figure 2. Stereoview of silyl ketene acetal **1**.

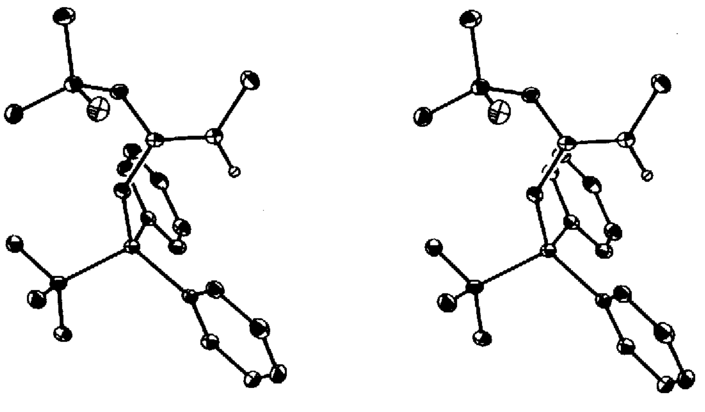
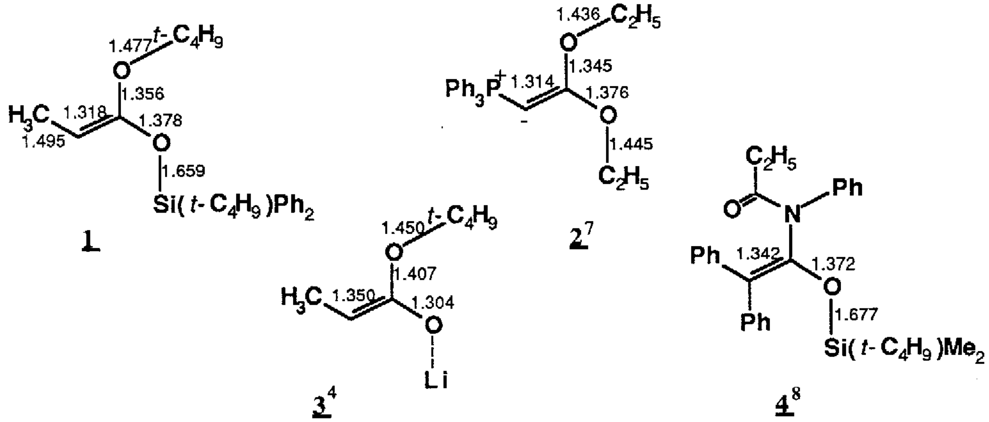


Figure 3. Bond distances (Å) in related structures.

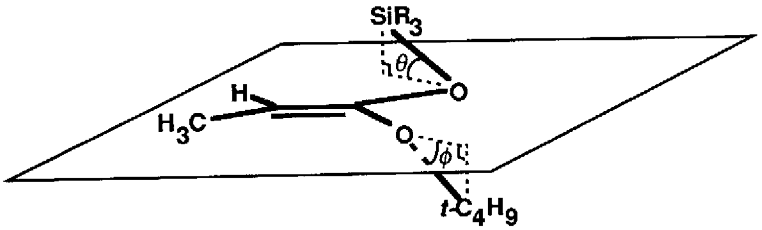


effect centered on the sp^2 carbon might contribute to the observed bond length differences (and the observed dihedral angles) cannot be confirmed with these data. It's notable that in the other molecules illustrated in Figure 3 those C-O bonds which are antiperiplanar to lone electron pairs are similarly lengthened.

Wilcox and Babston proposed that ketene acetals prepared from propanoate esters will take up "pin-wheel" type conformations in which the oxygen substituents would lie close to the plane defined by the alkene.^{9} The pin-wheel shape defined by acetal **1** is clearly revealed in the view presented in Figure 2. Figure 4 illustrates the non-planarity of ketene acetal **1**. The angle (θ, Figure 4) formed between bond Si1-O18 and the line formed by the projection of Si1-O18 to the plane is 31.6°. The corresponding angle for C21-O20 (ϕ, Figure 4) is 47.1°. These large oxygen substituents do *not* lie in the plane defined by the alkene but smaller substituents are likely to move closer to the plane.^{9} In fact, the carbons attached to the acetal oxygens in acetal **2** are very nearly in the plane defined by the alkene.

These are the first available data on the structure of any ketene acetal derived from a propanoate ester. These data should be helpful in attempts to model the structure of ketene acetals and/or parameterize force field calculations which may be used to explain the stereochemical outcome of reactions involving these important intermediates.

Figure 4. Illustration of out-of-plane placement of oxygen substituents in acetal **1**.



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References and Notes.

1. This work was carried out at the University of Texas at Austin.
2. Address questions concerning the structure determination to this author at the Department of Chemistry, University of Texas at Austin. Austin, TX 78712.
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5. Data were collected at 163 K. The crystal system is triclinic, space group P1 (No. 2). Lattice parameters as given in the text. A total of 10029 unique data were collected using the omega scan technique with a 2Θ range from 4.0 - 55.0° . Four reflections were remeasured every 96 reflections to monitor instrument and crystal stability. Maximum decay correction <1%.[10] Reflections with $F_o < 4\sigma(F_o)$ considered unobserved (2743 reflections). Structure solved by direct methods and refined by full-matrix least-squares procedures[11] with anisotropic thermal parameters for the non-H atoms. All H atoms were obtained from a ΔF map and refined with isotropic thermal parameters. Final R = 0.0453 for 7286 reflections, wR = 0.0398 (R for all reflections = 0.0717, wR for all reflections = 0.0419) and a goodness of fit = 1.563. There are only very minor differences in the geometry of the two crystallographically unique molecules. For example, the maximum difference in bond length between equivalent atoms is 0.01 Å and the maximum difference in bond angles is 2.9° and -2.0° for Si1-O18-C19 and Si1-C14-C15, respectively. There are slight differences in orientation of the phenyl rings between the two molecules. Neutral atom scattering factors were used for all atoms,[12,13] with anomalous-dispersion corrections for the non-H atoms.[14] Values for the linear absorption coefficient were taken from the International Table for X-ray Crystallography.[15] The least squares planes program was supplied by Cordes;[16] other computer programs are listed elsewhere.[17]
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