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The Effect of Protecting Groups on Chelation Control

S.D. Kahn,[†] G.E. Keck[§] and W.J. Hehre[†]*
Departments of Chemistry
University of California, Irvine, CA 92717
University of Utah, Salt Lake City, UT 84112

Abstract: Relative chelating abilities of alcohols, ethers and silyl ethers are rationalized in terms of the π accepting character of the group attached to oxygen. This in turn may be assessed by examination of the bond angle about oxygen.

Chelation is a practical means of controlling the course of asymmetric organic reactions.[1] The variety of applications of "chelation controlled" reactions has resulted in a considerable body of qualitative knowledge concerning the effect of substituents on the participation of a chelating oxygen. Specifically, alkyl substitution on oxygen is known to permit chelation with common Lewis acids, e.g., $MgBr_2$, $SnCl_4$ or $TiCl_4$, whereas substitution with trialkylsilyl aparently attenuates or even eliminates the ability of an oxygen to chelate.[2] While the latter observation contradicts the usual characterization of trimethylsilyl as a strong σ donor,[3] it is consistent with the ability of such groups to function as π acceptors.[4] Delocalization of the oxygen lone-pair electrons leads to a lowering of their energy, rendering them less available for external interactions.[5]

It is known[6] that metal-oxygen-carbon bond angles in alkoxy complexes of alkali, alkaline earth and early transition metals are linear or nearly so. These deviations (from the near-tetrahedral bond angles found in alcohols and ethers) arise from donation of the lone pairs on oxygen into empty p- or d-type orbitals on the metal. It is reasonable to suggest, therefore, that the bond angle about oxygen in ethers and ether analogues will mirror lone pair energy, i.e., the amount of oxygen π donation, and provide an indicator of chelation ability. The smaller the bond angle about oxygen, the better its ability to participate in chelation with external Lewis acids.

It follows from the ordering of calculated X-O-H bond angles (Table), that trialkylsilyl, mimicked by SiH_3, and trifluoromethyl ethers should be less subject to chelation than ethers or alcohols. Correspondingly, calculated C-O-X bond angles in 3-buten-2-ol,[7] and its methyl[8] and silyl[9] ethers suggest that the product stereochemistries in reactions of the silyl protected alcohol would be less affected by chelation imposed biases than those for either the free alcohol or the methyl ether.

It should be noted that the variation in chelating ability discussed herein is of electronic origin. Steric effects alone, while perhaps leading to abnormally large bond angles, should be of little consequence in determining the energetic disposition of the oxygen lone-pair orbitals. This, however, does not discount the possible shielding of the oxygen lone pairs by bulky substituents, thereby hampering chelation.

Table. Central bond angles of X-O-Y species.[a]

Molecule	3-21G[b]	6-31G*	Expt.
H_2O	107.6	105.5	104.5[c]
CH_3OH	110.4	109.4	108.0[d]
CF_3OH	114.8	110.3	-
SiH_3OH	128.8	119.0	-
LiOH	180.0	180.0	180.0[e]
$CH_2{=}CHCH(CH_3)OH$	110.2	-	-
$CH_2{=}CHCH(CH_3)OCH_3$	116.2	-	-
$CH_2{=}CHCH(CH_3)OSiH_3$	131.3	-	-

a) From fully optimized Hartree-Fock structures[10].

b) 3-21G$^{(*)}$ for molecules incorporating second-row elements.

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†University of California, §University of Utah

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