trophilic ring boron with ketonic oxygen (*anti* to the larger carbonyl appendage) and hydrogen transfer from the NBH₃⁻ unit to the carbonyl carbon via a six-membered cyclic transition state, following the path formulated in Chart I. This mechanistic picture accords with all the facts available. It unambiguously explains the observed absolute stereochemistry of the reductions. In addition the observed differences between **3** and **2** are readily understood, including (1) the slower formation of **3** from BH₃·THF relative to **2** from **1** (excess strain of the B=N π-bond at the 5,5-ring fusion of **3**), (2) the stronger coordination of **3** with BH₃·THF to form **4**, and (3) the higher enantioselectivities observed with **3**.

We believe that the mechanistic understanding gained in this work will stimulate further exciting advances in this important area of chemistry. Many applications of this new catalytic methodology in synthesis can be foreseen.[11]

Isolation and Characterization of a Stable Simple Enol

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Received March 5, 1987

Enols lacking functionality which confers special stability have been called "simple enols" and are generally unstable relative to their carbonyl tautomers.[1] Certain simple enols exhibit unexpected stability, but the underlying reasons are clouded by the paucity of detailed structural data.[1,2] We have isolated simple enol **2** and find it to possess unusual stability. Reported herein are the X-ray structures of ketone **1** and enol **2** which suggest that the stability of enol **2** results from factors which destabilize its ketone tautomer **1**.
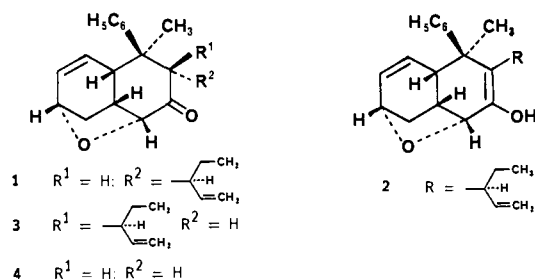
The synthesis of tricyclic ketone **1** has been reported.[3] The epimeric ketone **3** was of interest as an intermediate in a synthesis project. Surprisingly, treatment of ketone **1** in 5:1 CH₃OH/THF with 10 equiv of NaOCH₃ (25 °C, 2 h, Ar) followed by quenching with water afforded (instead of **3**) enol **2** in essentially quantitative yield. In solid or solution phase, enol **2** did not revert to ketones **1** or **3**. The structures of ketone **1** (Figure 1) and enol **2** (Figure 2) were confirmed by X-ray analysis. The relative energies of ketones **1** and **3** and enol **2** were determined by equilibration with 10 mol % NaOCH₃ in CD₃OD (sealed tube, 500 MHz PMR analysis), which required in excess of 20 h at 70 °C. The equilibrium ratio of **1:2:3** was found to be roughly 5:2:3,[4,5] which

(1) Hart, H. *Chem. Rev.* **1979**, *79*, 515. Hart, H.; Sasaoka, J. *J. Chem. Ed.* **1981**, *57*, 685.

(2) For well-characterized enols of the type first isolated by Fuson, see: (a) Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 1007. (b) Kaftory, M.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 1701. (c) Nugiel, D. A.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 3669.

(3) Pratt, D. V.; Hopkins, P. B. *Tetrahedron Lett.* **1987**, *28*, 3065.

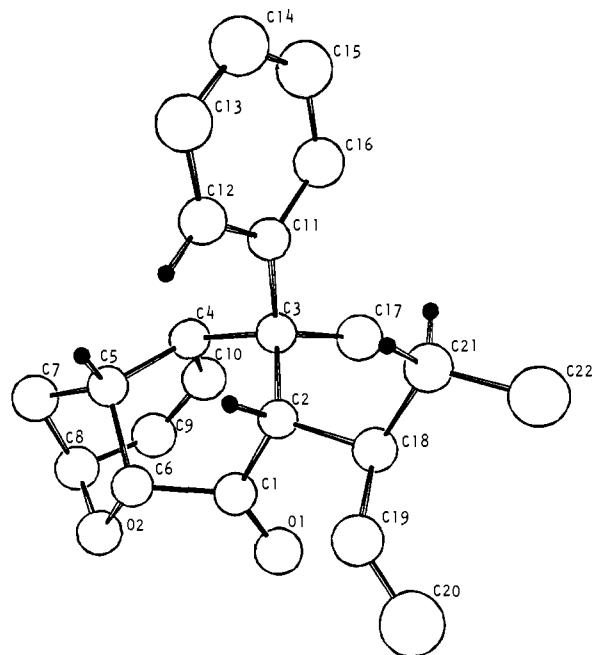(4) All compounds were characterized by IR, ¹H NMR (500 MHz), and MS.

Figure 1. X-ray structure of ketone **1**. Most hydrogens omitted for clarity.
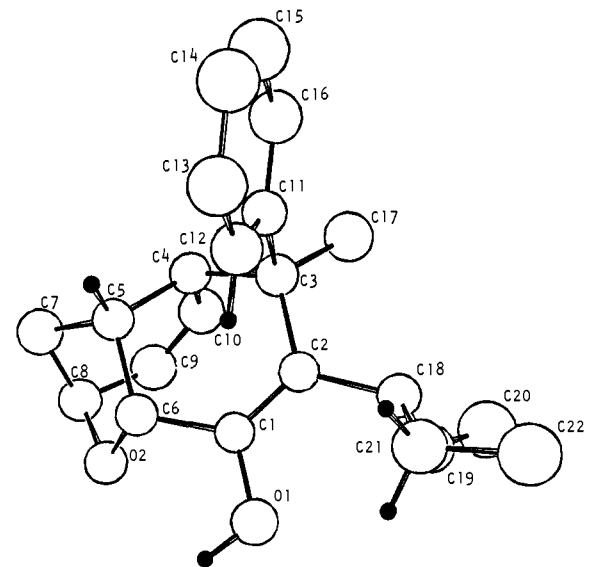
Figure 2. X-ray structure of enol **2**. Most hydrogens omitted for clarity.

corresponds to a free energy difference between enol **2** and ketones **1** and **3** of, respectively, 0.6 and 0.3 kcal/mol.

The X-ray structures of **1** and **2** suggest that the relative thermodynamic stability of enol **2** has its origin in steric and dipolar destabilization of ketones **1** and (presumably) **3** which is relieved on enolization.[1,2,6] Remarkable in the structure of ketone **1** is the sp³ bond angle C3–C2–C18 of 119.0° which results from van der Waals contact of methylene C21 with C11 of the phenyl ring (see Table I). This contact is relieved on enolization. Additionally, C2 of **1** is strained by contacts of phenyl-bound hydrogen H(C12) with H(C2) and H(C5). Enolization eliminates the H(C2)–H(C12) contact and permits torsional reorganization of the phenyl substituent to relieve the H(C5)–H(C12) contact.

Ketone **1** is further destabilized by dipole–dipole interaction of the carbonyl with the nearly eclipsed ether bridge. Not only does the enol functional group have a lower dipole moment,[7] but the torsional angle with the adjacent C–O bond increases in **2**.

(5) The same ratio was obtained starting with **1**, **2**, or **3**.

(6) Miller, A. R. *J. Org. Chem.* **1976**, *41*, 3599.

(7) Saito, S. *Chem. Phys. Lett.* **1976**, *42*, 399.

Table I. Selected Distances (Å) and Angles (deg) from **1** and **2**

	1	2
Bond Distances		
O1–C1	1.225 (3)	1.377 (5)
C1–C2	1.496 (4)	1.330 (6)
C3–C4	1.589 (4)	1.570 (7)
Nonbonded Distances		
H(C2)–H(C12)	2.038	
H(C5)–H(C12)	2.297	2.767
C11–C21	3.268	4.342
Bond Angles		
C1–C2–C3	105.3 (2)	120.0 (4)
C1–C2–C18	112.2 (3)	121.5 (4)
C1–C2–H(C2)	106 (2)	
C3–C2–C18	119.0 (2)	118.5 (3)
C3–C2–H(C2)	105 (2)	
C18–C2–H(C2)	108 (2)	
Torsional Angles		
O1–C1–C2–C18	27.9	4.0
O1–C1–C6–O2	16.1	58.1
C18–C2–C3–C11	82.4	83.1
C18–C2–C3–C17	–41.8	–39.1
C1–C2–C18–C19	58.6	–69.7
C2–C3–C11–C12	45.6	25.1

In aqueous solution, cyclohexanone is roughly 6 kcal/mol more stable than the corresponding enol.[8] Molecular mechanics calculations (MM2) on the X-ray derived conformations find roughly this amount of destabilization of ketone **1** relative to enol **2**.[9] The calculated strain due to angle distortion at C2 and nonbonded van der Waals contacts of H(C2) and methylene C21 in ketone **1** totaled 3.9 kcal/mol.[10] A further 2.5 kcal/mol of dipole–dipole destabilization of ketone **1** was predicted for the interaction of the carbonyl group with the ether bridge C–O bonds and lone pairs.[11] These effects were eliminated or substantially reduced in the calculated structure of enol **2**.[12]

5   R¹ = H; R² = —CH₃
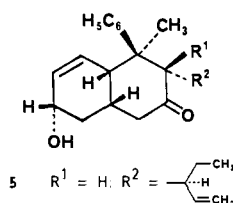
Experimental support for destabilization of **1** by these effects was obtained. Neither **4** nor **5** formed an isolable enol when exposed to excess NaOCH₃ in CD₃OD, although the hydrogens α to the carbonyls were exchanged for deuterium. The failure of both **4** and **5** to form a stable enol substantiates the critical roles played by the C2 side chain and ether bridge.

A New Route to Trimethylsilylated Spherosilicates: Synthesis and Structure of [Si₁₂O₁₈](OSiMe₃)₁₂, D₃ₕ-[Si₁₄O₂₁](OSiMe₃)₁₄, and C₂ᵥ-[Si₁₄O₂₁](OSiMe₃)₁₄

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Received February 9, 1987

Molecular polyhedral silicates (spherosilicates) whose anionic oxygen atoms have been protected by trimethylsilyl groups are convenient molecular species for examining the properties of isolated polysilicate cage frameworks.[2] At present, three such species are known: the trigonal prismatic [Si₆O₉](OSiMe₃)₆,[3] cubic [Si₈O₁₂](OSiMe₃)₈,[4] and pentagonal prismatic [Si₁₀O₁₅]-(OSiMe₃)₁₀[5] molecules. The family of trimethylsilylated spherosilicates (Me₃SiOSiO₁.₅)ₙ has been restricted to n = 6, 8, and 10 for purely practical reasons. These materials are prepared by trimethylsilylation of the silicate anions SiₙO₂.₅ₙⁿ⁻, and soluble anions are known only for n = 6,[3] 8,[4] and 10.[5] We describe here a new route to trimethylsilylated spherosilicates that utilizes hydridosiloxane precursors and report the synthesis, structure, and stability of three new compounds prepared by this route, [Si₁₂O₁₈](OSiMe₃)₁₂, D₃ₕ-[Si₁₄O₂₁](OSiMe₃)₁₄, and C₂ᵥ-[Si₁₄O₂₁](OSiMe₃)₁₄.

Polyhedral hydridosiloxane precursors were isolated from a mixture of species (HSiO₁.₅)ₙ, n = 8, 10, 12, 14, and 16, prepared by a method previously described by Frye and Collins.[6] Gel permeation chromatography was used to obtain a fraction of this material containing largely the n = 12, 14, and 16 species. Crystalline [Si₁₂O₁₈]H₁₂,[7] **1**, was separated from this mixture by slow evaporation of a saturated pentane solution. When a hot, saturated 4:1 V/V acetonitrile/tetrahydrofuran solution of the residual material was cooled to room temperature, crystalline [Si₁₄O₂₁]H₁₄,[7] **2**, was obtained. The material remaining was then separated into three fractions by using preparative gas chromatography. The central fraction contained predominantly compound **2** and a second [Si₁₄O₂₁]H₁₄ isomer,[8] **3**, according to capillary gas chromatography/mass spectrometry. Following the procedure

(8) (a) Schwarzenbach, G.; Witter, Ch. *Helv. Chim. Acta* **1947**, *30*, 669. (b) Bell, R. P.; Smith, P. W. *J. Chem. Soc. B* **1966**, 241.

(9) Although the MM2P force field is more appropriate for calculations on enols, use of the latter is unlikely to significantly alter these results, see: (a) Dodziuk, H.; von Voithenberg, H.; Allinger, N. L. *Tetrahedron* **1982**, *38*, 2811. (b) Biali, S. E.; Meyer, A. Y.; Rappoport, Z.; Yuh, Y. H. *J. Org. Chem.* **1985**, *50*, 3919.

(10) Excluding 1,4-nonbonded interactions.

(11) The calculated dipole–dipole interaction energies should be taken as indicative only, since the magnitude varies inversely with the dielectric of the medium, an unknown quantity; MM2 uses a default dielectric of 1.5. Additionally, MM2 is not adequately parameterized in the dipole–dipole computation to deal with enols.⁹ On the basis of the relative dipole moments of carbonyl (2.6 D) and enol (1.0 D⁸), this term is clearly reduced on enolization.

(12) The available spectroscopic data are at this time insufficient to support or refute the possibility that enol **2** benefits in the solution phase from an intramolecular hydrogen bond to the ether bridge or side chain double bond.

(1) (a) University of Illinois. (b) Crystalytics Company.

(2) Voronkov, M. G.; Lavrent'yev, V. I. *Top. Current Chem.* **1982**, *102*, 199.

(3) (a) Hoebbel, D.; Garzo, G.; Engelhardt, G.; Ebert, R.; Lippmaa, E.; Alla, M. *Z. Anorg. Allg. Chem.* **1980**, *465*, 15. (b) Smolin, Yu. I.; Shepelev, Yu. F.; Ershov, A. S.; Hoebbel, D.; Wieker, W. *Sov. Phys. Crystallogr.* **1984**, *29*, 421.

(4) (a) Hoebbel, D.; Wieker, W. *Z. Anorg. Allg. Chem.* **1971**, *384*, 43. (b) Smolin, Yu. I.; Shepelev, Yu. F.; Pomes, R. *Khim. Silik. Oksidov* **1982**, 68.

(5) Hoebbel, D.; Wieker, W.; Franke, P.; Otto, A. *Z. Anorg. Allg. Chem.* **1975**, *418*, 35.

(6) Frye, C. L.; Collins, W. T. *J. Am. Chem. Soc.* **1970**, *92*, 5586.

(7) For spectroscopic/analytical data, see paragraph at end of paper regarding Supplementary Material.

(8) GC/MS on a 30-m Alltech DB-5 capillary column with a temperature ramp of 3 °C/min from 100 °C to 200 °C and carrier gas He at 15 psig head pressure showed two major components at 23.33 and 23.75 min with *m/z* 741 (M⁺ – H).