Alkyl- and Silyl-Substituent Effects on Keto-Enol Equilibria and the Structures of Simple Aliphatic Enols. A Theoretical ab Initio Study[§]
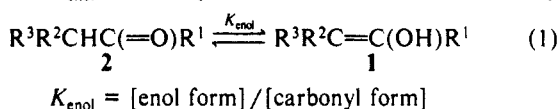
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Abstract: Ab initio molecular orbital theory was used to study the following enol–carbonyl pairs: $H_2C=C(OH)R$ (4)–$CH_3C(=O)R$ (5) [R = H, Me, Et, *i*-Pr, *t*-Bu, SiH_3, $SiMe_3$], $CH_3CH=C(OH)R$ (6*E* and 6*Z*)–$CH_3CH_2C(=O)R$ (7) [R = H, Me, Et, *i*-Pr, *t*-Bu], $(CH_3)_2C=C(OH)R$ (8)–$(CH_3)_2CHC(=O)R$ (9) [R = H, Me]. Geometries were optimized with the 3-21G basis set, and for most molecules single-point 6-31G* calculations were also performed. For 4 and 5 (R = H, Me) geometry optimizations were carried out also at 6-31G* and 6-31G** and for R = H also at MP2/6-31G*. In the most stable conformation of the carbonyl compounds a C–H or preferably a C–C bond (Si–H and Si–C bonds, respectively, in the α-silyl ketones) eclipses the carbonyl bond. All the enols adopt the syn conformation (i.e., ∠H—O—C=C = 0°), but Δ*E*(syn–anti) is smaller in the 6*Z* series than in the 6*E* or the 4 series. In the 6*Z* series the C–H bond of the β-methyl group eclipses the C=C bond. Our best calculated Δ*E*(4a–5a) and Δ*E*(4b–5b) energy differences are 14.9 (at MP4SDTQ/6-31G**//6-31G**+ZPE) and 17 kcal mol⁻¹, respectively, but a larger MP2/6-311++G**//6-31G* calculation gives Δ*E*(4a–5a) = 11.1 kcal mol⁻¹ (ref 30a). Addition of polarization functions on hydrogen and further splitting of the valence shell lowers Δ*E* by ca. 7.3 kcal mol⁻¹, but electron correlation has a small effect on Δ*E*. The best theoretical Δ*E* values are higher by 2–3 kcal mol⁻¹ than gas-phase experimental values. Comparison with experimental data shows that Δ*E* values of simple enol–ketone pairs are smaller (K_{enol} larger) by 1–2 kcal mol⁻¹ in water than in the gas phase. An α-alkyl substituent increases Δ*E*(4–5) (6-31G*//3-21G) by 2.8 (Me), 3.9 (Et), 2.7 (*i*-Pr), and 2.7 (est.) (*t*-Bu) kcal mol⁻¹, but an α-silyl substituent decreases Δ*E*(4–5) by ca. 6 kcal mol⁻¹. These results are in good agreement with recent K_{enol} values in solution. Enols 6*Z* are more stable than the isomeric 6*E*, except for 6*E* (R = H), which is by 0.5 kcal mol⁻¹ more stable. Δ*E*(6*E*–6*Z*) increases with the steric bulk of α-R, up to 4.8 kcal mol⁻¹ for R = *t*-Bu. A β-methyl substituent increases Δ*E*, but in the *E* series the effect is quite small (ca. 1 kcal mol⁻¹, except for α-R = *t*-Bu). These results contrast with experimental data that indicate a decrease in Δ*E* by β-methyl substitution. The paper points to several computational–experimental discrepancies and calls for more accurate gas-phase measurements as well as more sophisticated calculations.

Introduction

Simple enols (1), i.e., those where the substituents R¹, R², and R³ are not strongly electron withdrawing, are usually regarded as short-lived species.[1] Nevertheless, they are transient intermediates in hydration of acetylenes, acid-catalyzed halogenations, and aldol condensations and other electrophilic reactions of aldehydes and ketones (2).[2] Studies of the keto–enol equilibria of simple enols are therefore of interest. However, until recently the reported K_{enol} values (eq 1) were inaccurate due to the very

$$R^3R^2CHC(=O)R^1 \xrightleftharpoons{K_{enol}} R^3R^2C=C(OH)R^1 \quad (1)$$
$$\mathbf{2} \qquad\qquad\qquad \mathbf{1}$$

$$K_{enol} = [\text{enol form}]/[\text{carbonyl form}]$$

low enol concentrations at equilibrium.[1a] Recently, these studies gained new momentum due to two major developments. First, new approaches and methods enabled generation and observation of short-lived enols that are thermodynamically unstable relative to their carbonyl isomers.[3] This allows the accurate calculation of K_{enol} values for many enols,[1c,4] including those of acetaldehyde,[4b] acetone,[4c] isobutyraldehyde,[4d] acetophenones,[4e] and cyclic ketones.[4c] The K_{enol} values in water are mostly <10⁻⁴, i.e., the ketones are much more stable than the enols.[1c,4] Second, a group of thermodynamically and kinetically stable long-lived crowded polyaryl-substituted enols, e.g., trimesitylethenol (3g), was thoroughly investigated,[5] following earlier work by Fuson[6] and their K_{enol} values in hexane were found to be 0.01–80;[5,7] i.e., several of these enols are more stable than the ketones. Systems substituted by β-aryl groups less bulky than mesityl cover the gap in K_{enol} values between these two groups.[8]

Quantitative investigation of substituent effects on K_{enol} are not numerous.[1c,e] In solution, both polar and resonance effects in-

fluence K_{enol}. Electron-withdrawing substituents in the aryl group of acetophenones, ArCOCH₃, increase K_{enol}.[4a] log K_{enol} correlates with σ⁺ (ρ⁺ = 0.65 in hexane) for systems 3a[7c] and with σ (ρ = 0.76 in DMSO) for 2-arylpropanals.[8a] A plot of log K_{enol} for 3b–3f vs Taft's steric parameter E_s gives a linear negative slope, i.e., the

(1) (a) For earlier reviews on enols see: Wheland, G. W. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1960; pp 663–702, Forsen, S.; Nilsson, M. In *The Chemistry of the Carbonyl Group*; Zabicky, J., Ed., Interscience: New York, 1970; Vol. 2, pp 158–240. (b) For a comprehensive treatment, see: *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley: Chichester, 1990. (c) For recent reviews on enolization and K_{enol} values see: Toullec, J. *Adv. Phys. Org. Chem.* **1982**, *18*, 1. Also see ref 1b, Chapter 6. (d) For reviews on simple enols see: Hart, H. *Chem. Rev.* **1979**, *79*, 515. Hart, H.; Sasaoka, M. *J. Chem. Educ.* **1980**, *57*, 685. (e) Guthrie, J. P., ref 1b, Chapter 2. (f) Kresge, A. J. *CHEMTECH* **1986**, *16*, 250.

(2) E.g.: March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; pp 530, 683, and 834.

(3) Recent reviews: (a) Capon, B.; Guo, B. Z.; Kwok, F. C.; Siddhanta, A. K.; Zucco, C. *Acc. Chem. Res.* **1988**, *21*, 135. (b) Capon, B., ref 1b, Chapter 5.

(4) (a) For a review see: Keeffe, J. R.; Kresge, A. J., ref 1b, Chapter 7. (b) Chiang, Y.; Hojatti, M.; Keeffe, J. R.; Kresge, A. J.; Schepp, N. P.; Wirz, J. *J. Am. Chem. Soc.* **1987**, *109*, 4000. (c) Keeffe, J. R.; Kresge, A. J.; Schepp, N. P. *Ibid.* **1988**, *110*, 1933. (d) Chiang, Y.; Kresge, A. J.; Walsh, P. A. *Ibid.* **1982**, *104*, 6122. (e) Dubois, J. E.; El-Alaoui, M.; Toullec, J. *Ibid.* **1981**, *103*, 5393. Toullec, J. *Tetrahedron Lett.* **1984**, *25*, 4401.

(5) For reviews see: (a) Rappoport, Z.; Biali, S. E. *Acc. Chem. Res.* **1988**, *21*, 442. (b) Hart, H.; Rappoport, Z.; Biali, S. E., ref 1b, Chapter 8.

(6) E.g.: (a) Fuson, R. C.; Rowland, S. P. *J. Am. Chem. Soc.* **1943**, *65*, 992. (b) Fuson, R. C.; Southwick, P. L.; Rowland, S. P. *Ibid.* **1944**, *66*, 1109. (c) Fuson, R. C.; Armstrong, L. J.; Chadwick, D. H.; Kneisley, J. W.; Rowland, S. P.; Shenk, W. J.; Soper, Q. F. *Ibid.* **1945**, *67*, 386. (d) Fuson, R. C.; Forster, R. E.; Shenk, W. J.; Maynert, E. W. *Ibid.* **1945**, *67*, 1937. (e) Fuson, R. C.; Chadwick, D. H.; Ward, M. L. *Ibid.* **1946**, *68*, 389.

(7) (a) Nugiel, D. A.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 3669. (b) Biali, S. E.; Rappoport, Z. *Ibid.* **1985**, *107*, 1007. (c) Nadler, E. B.; Rappoport, Z. *Ibid.* **1987**, *109*, 2112.

(8) (a) Ahlbrecht, H.; Funk, W.; Reiner, M. T. *Tetrahedron* **1976**, *32*, 479. (b) Argile, A.; Carey, A. R. E.; Fukata, G.; Harcourt, M.; More O'Ferrall, R. A.; Murphy, M. G. *Isr. J. Chem.* **1985**, *26*, 303. (c) Chiang, Y.; Kresge, A. J.; Krogh, E. T. *J. Am. Chem. Soc.* **1988**, *110*, 2600. (d) Chiang, Y.; Kresge, A. J.; Walsh, P. A.; Yin, Y. *ibid.* **1989**, *111*, 969.

bulkiest R gives the smallest K_{enol} value.[5a,7a] However, for R = aryl, $K_{enol}(\alpha\text{-mesityl}) > K_{enol}(\alpha\text{-Ph})$,[7b,c] suggesting that the steric bulk of the α-substituent might affect K_{enol} in opposite directions when R is aliphatic or aromatic.


3

a, R = meta- and para-substituted aryl; **b**, R = H; **c**, R = Me; **d**, R = Et; **e**, R = *i*-Pr; **f**, R = *t*-Bu; **g**, R = Mes; **h**, R = SiMe₃

Less was known until recently about alkyl-substituted enols.[4c] In water, K_{enol} for acetone is two orders of magnitude lower than that for acetaldehyde.[4b,c] The appreciably higher K_{enol} value of isobutyraldehyde than of acetaldehyde, suggests that a larger C_β-alkyl group increases K_{enol}.[4c,d] In methyl ketones two β-methyl groups increase the enol stability but less than for the aldehydes.[4c] Tureček et al. reported similar methyl effects on K_{enol} in the gas phase.[9]

A correlation between log K_{enol}(**3**) in hexane and log K_{enol} ($H_2C=C(OH)R$) in water was found in 1987, and it was suggested that it can be used to predict unavailable K_{enol} values for aliphatic enols.[10] However, due to the scarcity of experimental data it could be examined only for five systems.[10] The lack of sufficient data for evaluating the generality of this correlation initiated our computational study. In parallel, Kresge's group reported that the K_{enol} values for **4b–e** are almost constant[4c] and that they do not show the dependence on steric effects found for enols **3b–f**,[7a] establishing that the above correlation[10] resulted from the limited data that were available. We have now reached the same conclusions by our MO calculations.

Systems **4–9** were selected for the calculations in order to evaluate the following points: (a) The first need was to establish the level of theory required for reproducing the limited available experimental gas-phase data of simple enol/aldehyde or enol/ketone pairs.[9,11,12] This will enable predictions of properties such as molecular geometry and enol–carbonyl energy differences (or K_{enol} values). (b) Most K_{enol} values for simple aliphatic enols are
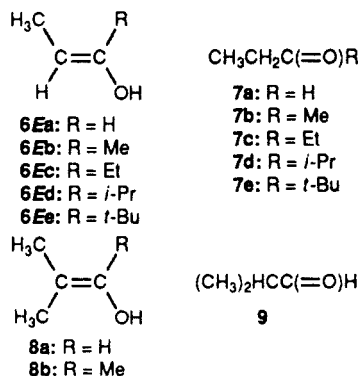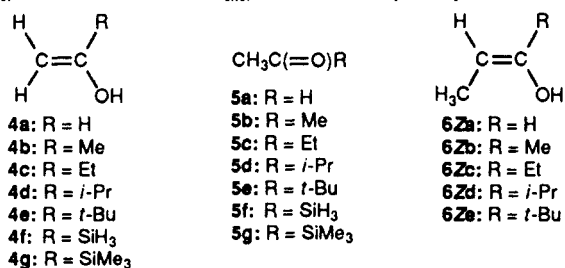
in water[4c] and alkyl effects on the inherent K_{enol} values are unknown (except for **4b–5b**). Comparison of calculated K_{enol} values (which refer to the gas phase) with the corresponding K_{enol}(water) values can provide data on the solvent effect on K_{enol}. (c) Calculations of the (enol–carbonyl) energy differences enable the study of simple α-alkyl- and β-methyl-substituent effects on the gas-phase intrinsic K_{enol} values and the assessment of the contributions of the keto and the enol components. (d) The calculated K_{enol} values for **6Za–e/7a–e** are useful in a qualitative interpretation of the R/β-mesityl steric interactions in series **3**. (e) The conformation of ketones is of current interest,[13] and ketones **5e–g** and **7c–e** will add new conformational data. (f) Both a microwave spectrum in the gas phase[14] and NMR data in slightly aqueous acetone[15] establish a syn conformation of the C=COH moiety of **4a**. However, NMR data suggest a predominant anti conformation for **6Za** and **8a**, which have *cis*-OH and methyl substituents.[15] In CCl₄[16] and in the solid state,[17] **3a–g** exist in an intramolecularly $\pi(\beta'\text{-Mes})\text{–OH}$ hydrogen-bonded syn conformation except for **3b** which is hydrogen bonded to EtOH of crystallization.[17b] The calculations can reveal if the conformational change for **6Za** and **8a** reflects a solvation effect. (g) In solid **3c–f** a C–H or a C–C bond of the R group eclipses the double bond.[17b] Does this apply for less-congested enols such as **4** and **6**? (h) Can a substituent that is not strongly electron withdrawing be found that will increase K_{enol} substantially? Our earlier studies[18a–c] suggested that this may be achieved by silyl substitution. The pairs **4f–5f** and **4g–5g** were therefore studied.[18d]

Ab initio calculations have previously been performed on several keto–enol pairs.[19–22] The calculated energy difference ΔE(vinyl alcohol–acetaldehyde) ranged from 10.4 to 19.5 kcal mol⁻¹.[20] Computations for the pairs **4b–5b**[21] and **6a–7a**[22b] show qualitatively (with one exception[20f]) that an α-alkyl group increases ΔE-(enol–keto), whereas a β-alkyl substituent reduces it.[22b] Note that an increase in ΔE(enol–carbonyl) indicates increased relative stability of the carbonyl compound and thus a smaller K_{enol}.

(13) (a) Wiberg, K. B.; Murcko, M. A. *J. Comput. Chem.* **1988**, *9*, 488. (b) Wiberg, K. B. *J. Am. Chem. Soc.* **1986**, *108*, 5817. (c) Wiberg, K. B.; Martin, E. *Ibid.* **1985**, *107*, 5035 and references therein.

(14) (a) Saito, S. *Chem. Phys. Lett.* **1976**, *42*, 399. (b) Saito, S. *Pure Appl. Chem.* **1978**, *50*, 1239. (c) Rodler, M.; Bauder, A. *J. Am. Chem. Soc.* **1984**, *106*, 4025. (d) Kaushik, V. K. *Chem. Phys. Lett.* **1977**, *49*, 255.

(15) Capon, B.; Siddhanta, A. K. *Tetrahedron Lett.* **1982**, *23*, 3189; *J. Org. Chem.* **1984**, *49*, 80.

(16) (a) Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 5641. (b) Nadler, E. B.; Rappoport, Z. *Ibid.* **1989**, *111*, 213. (c) Rappoport, Z.; Nugiel, D. A.; Biali, S. E. *J. Org. Chem.* **1988**, *53*, 4814.

(17) (a) Kaftory, M.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 1701. (b) Kaftory, M.; Nugiel, D. A.; Biali, S. E.; Rappoport, Z. *Ibid.* **1989**, *111*, 8181.

(18) (a) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806. (b) Apeloig, Y.; Stanger, A. *J. Org. Chem.* **1982**, *47*, 1462; **1983**, *48*, 5413. (c) Stanger, A. Ph.D. Thesis, Technion, Haifa, Israel, 1985. (d) For a preliminary report see: Nadler, E. B.; Rappoport, Z.; Arad, D.; Apeloig, Y. *J. Am. Chem. Soc.* **1987**, *109*, 7873.

(19) For a comprehensive review on calculations of enols see: Apeloig, Y., ref 1b, Chapter 1.

(20) For previous ab initio calculations of the acetaldehyde–vinyl alcohol pair see: (a) Heinrich, N.; Koch, W.; Frenking, G.; Schwarz, H. *J. Am. Chem. Soc.* **1986**, *108*, 593 and references therein. (b) Nguyen, M. T.; Hegarty, A. F.; Ha, T.-K.; De Mare, G. R. *J. Chem. Soc., Perkin Trans. 2* **1986**, 147. (c) Ventura, O. N.; Lledos, A.; Bonaccorsi, R.; Bertran, J.; Tomasi, J. *Theor. Chim. Acta* **1987**, *72*, 175. (d) Schleyer, P. v. R. *Pure Appl. Chem.* **1987**, *59*, 1647. (e) Greenberg, A.; Stevenson, T. A. *J. Am. Chem. Soc.* **1985**, *107*, 3488. (f) Noack, W.-E. *Theor. Chim. Acta* **1979**, *53*, 101. (g) Bouma, W. J.; Radom, L. *J. Mol. Struct.* **1978**, *43*, 267. (h) Rodwell, W. R.; Bouma, W. J.; Radom, L. *Int. J. Quantum Chem.* **1980**, *18*, 107. (i) Kunttu, H.; Dahlquis, M.; Murto, J.; Rasanen, M. *J. Phys. Chem.* **1988**, *92*, 1945. (j) Hehre, W. J.; Lathan, W. A. *J. Chem. Soc., Chem. Commun.* **1972**, 771.

(21) For previous ab initio calculations of the acetone–propen-2-ol pair see: (a) Siggel, M. R. F.; Thomas, T. D.; Saethre, L. F. *J. Am. Chem. Soc.* **1988**, *110*, 91. (b) Bowers, P.; Schafer, L. *J. Mol. Struct.* **1980**, *69*, 233. (c) See also refs 20a, 20f, and 20j.

(22) For calculations of other substituted enols see: Enols of type XCH=CHOH, X = CN, NO, NO₂, CHO: (a) Bouma, W. J.; Radom, L. *Aust. J. Chem.* **1978**, *31*, 1649. (b) X = Li, BeH, BH₂, Me, NH₂, OH, F: Bouma, W. J.; Radom, L. *Ibid.* **1978**, *31*, 1167. (c) X = N₂⁺: Ballard, M. J.; Bouma, W. J.; Radom, L.; Vincent, M. A. *Ibid.* **1979**, *32*, 1401. (d) For recent calculations of cyclobut-1-en-1-ol see: Plant, C.; Spencer, K.; Macdonald, J. N. *J. Chem. Soc., Faraday Trans. 2* **1987**, *83*, 1411. (e) See also refs 20a, 20f, and 21b.

(9) Tureček, F.; Brabec, L.; Korvola, J. *J. Am. Chem. Soc.* **1988**, *110*, 7984.

(10) Rappoport, Z. *J. Am. Chem. Soc.* **1987**, *109*, 4730.

(11) (a) Holmes, J. L.; Terlouw, J. K.; Lossing, F. P. *J. Phys. Chem.* **1976**, *80*, 2860. (b) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1982**, *104*, 2648. (c) Holmes, J. L.; Lossing, F. P. *Ibid.* **1980**, *102*, 1591.

(12) (a) Tureček, F.; Havlas, Z. *J. Org. Chem.* **1986**, *51*, 4066. (b) Hehre, W. J.; Pollack, S. K. *J. Am. Chem. Soc.* **1977**, *99*, 4845. (c) Tureček, F. *J. Chem. Soc., Chem. Commun.* **1984**, 1374. (d) Iraqi, M.; Pri-Bar, I.; Lifshitz, C. *Org. Mass Spectrom.* **1986**, *21*, 661.
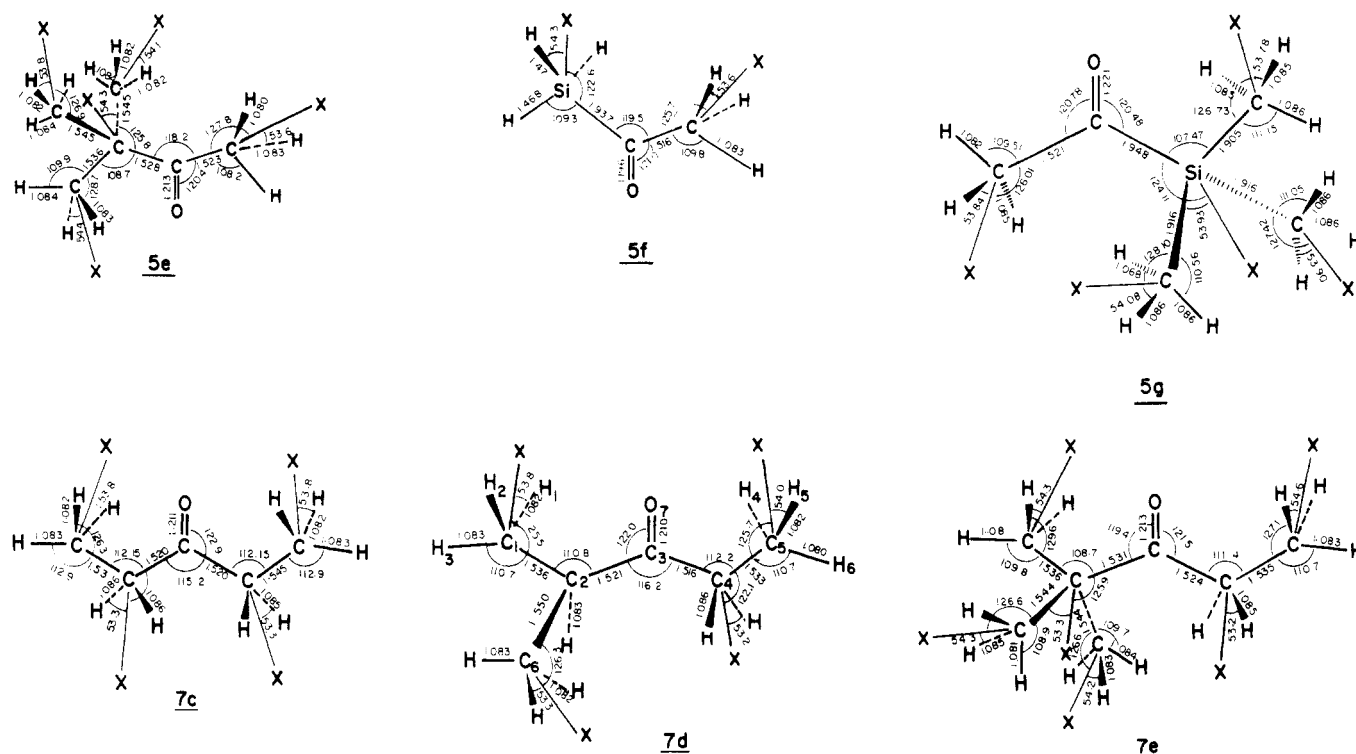
Figure 1. 3-21G optimized geometries of ketones **5e**, **5f**, **5g**, **7c**, **7d**, and **7e** (C_s symmetry was not assumed but geometry optimization gave C_s structures except for **7d**). X is a "dummy atom" located on the bisectors of the HCH, HSiH, or CCC angles. For **7d** the dihedral angles (deg) are as follows: $C_1C_2C_3O_7 = 30.7$; $C_2C_3C_4C_5 = 173.5$; $O_7C_3C_4C_5 = 5.3$; $H_3C_1C_2C_3 = 174.7$.

Methods

We have used standard ab initio methods[23] as implemented in the Gaussian 82 series of programs.[24] Full geometry optimizations were generally carried out with analytical techniques[23,24] and the split valence 3-21G basis set.[25] For each compound several possible conformations were calculated and all minima on the potential energy surface were properly identified.[23,24] For **4a-5a** and **4b-5b** geometry optimizations were also carried out with the polarized 6-31G* and 6-31G** (for **4a-5a**) basis sets and at MP2 6-31G* (for **4a-5a**).[26] For most molecules single-point 6-31G* calculations were carried out at the 3-21G optimized geometries. The effect of correlation energy was evaluated for some of the smaller molecules by using the Moller-Plesset perturbation theory up to fourth order (MP4).[27] Zero-point energies for **4a-5a** and **4b-5b** were evaluated at the 3-21G level.[23,24] We use the common notation,[23] e.g., MP3/6-31G*//3-21G denotes a single-point MP3/6-31G* calculation at the 3-21G optimized geometry. Total energies of all molecules calculated in this study are given in the supplementary material.

Results and Discussion

A. Geometries. 1. Carbonyl Compounds. The geometries and conformations of simple acyclic aldehydes and ketones were discussed by Wiberg et al.[13] However, ketones **5e-g** and **7c-e** were not previously calculated, and their most important geometrical parameters are presented in Figure 1. In the most stable conformation of the carbonyl species studied a C—H bond (when one substituent is Me) or a C—C bond eclipses the C=O bond, as shown in **10**. The origin of this preference was hitherto discussed.[13c] In analogy, in **5f** and **5g** a Si—H or a Si—C bond, respectively, eclipses the C=O bond. When one β-substituent

(23) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

(24) GAUSSIAN 82 ("Release A"): Binkley, J. S.; Whiteside, R. A.; Raghavachari, K.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Frisch, M. J.; Kahn, L. R.; Pople, J. A. Carnegie-Mellon University: Pittsburg, 1982.

(25) (a) Binkely, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *Ibid.* **1982**, *104*, 2797.

(26) (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213; *Chem. Phys. Lett.* **1972**, *66*, 217. (b) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(27) (a) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 1618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.
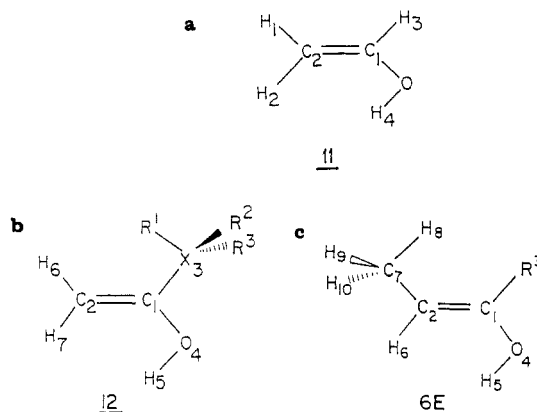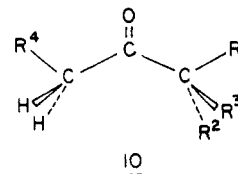
Figure 2. Atom and group numberings for (a) enol **4a** (geometrical parameters in Table I), conformation **11**, (b) enols **4b-g** (geometrical parameters in Table II), conformation **12**, (c) enols **6Ea-e** and **6Za-e** (geometrical parameters in Table III). Only **6E** is shown, but the same numbering applies to the **6Z** enols.

is Et, a C—C bond eclipses the C=O bond in preference to a C—H bond; e.g., the most stable conformation of 2-butanone (**5c**) is **10** (R^1 = Me; $R^2 = R^3 = R^4$ = H). The conformation in which the hydrogen eclipses the C=O bond, i.e., **10** ($R^1 = R^2 = R^4$ = H; R^3 = Me) is 2.7 kcal mol⁻¹ (3-21G) higher in energy. In the most stable conformation of 3-pentanone (**7c**) two C—C bonds eclipse the C=O bond (cf. **10**: $R^1 = R^4$ = Me; $R^2 = R^3$ = H). In 3,3-dimethyl-2-butanone (**5e**) the rotation barrier around the t-Bu—C=O bond is 1.27 kcal mol⁻¹ (3-21G); conformations with R^1CCO dihedral angles of 0° (cf. **10**: $R^1 = R^2 = R^3$ = Me; R^4 = H) and 180° are the lowest and highest points, respectively, along the rotation path.

Table I. Optimized Geometries of Vinyl Alcohol (**4a**) at Various Theoretical Levels[a]

geometrical parameter[b]	theoretical level						
	3-21G	4-31G	6-31G*	6-31G**	MP2/6-31G*	MP2/6-31G**[c]	exp[d]
distance, Å							
$C_1=C_2$	1.313	1.314	1.318	1.317	1.336	1.335	1.326
C_1-O	1.376	1.370	1.347	1.346	1.364	1.365	1.372
C_2-H_1	1.069	1.069	1.077	1.077	1.085	1.076	1.078
C_2-H_2	1.073	1.073	1.073	1.073	1.081	1.082	1.086
C_1-H_3	1.069	1.067	1.073	1.074	1.085	1.080	1.097
$O-H$	0.965	0.951	0.948	0.944	0.974	0.966	0.960
angle, deg							
$C_1C_2H_1$	120.4	120.5	122.4	122.2	122.3	119.9	119.5
$C_1C_2H_2$	122.5	122.6	120.1	120.0	120.0	122.1	121.7
$C_2C_1H_3$	122.7	123.5	122.4	122.2	122.6	122.7	129.1[e]
C_2C_1O	127.4	126.5	127.0	126.9	126.9	126.8	126.2
H_4OC_1	112.7	114.9	110.4	110.6	108.4	108.1	108.3

[a] For atom numbering see Figure 2a. [b] The molecule is essentially planar and thus dihedral angles are not given. The $H_4OC_1C_2$ dihedral angle is 0°. [c] From ref 20i. [d] From ref 14c. [e] 123.8° according to ref 14a.

2. Enols.

The geometry of vinyl alcohol (**4a**) was optimized at several theoretical levels ranging from 3-21G to MP2/6-31G*. The results are presented in Table I, which also includes the most recent experimental microwave (MW) structure of **4a**[14c] and a recent MP2/6-31G** optimized structure.[20i] Atom numbering is given in Figure 2a, structure **11**. At all levels of calculations **4a** is essentially planar and more stable in the syn conformation, in which the O—H bond eclipses the C=C bond as in structure **11** (Figure 2a) MW data,[14] NMR data in slightly aqueous acetone,[15] and previous calculations[20] lead to the same conclusion. The higher stabilities of conformations in which a hydrogen eclipses an adjacent C=C or a C=O bond have been discussed previously.[13c]

We find good agreement between the best calculated geometries, i.e., at MP2/6-31G* and MP2/6-31G**, and the experimental MW structure.[14] The calculated bond lengths and angles are within (and generally smaller than) 0.01 Å and 1°, respectively, of the experimental values.[14c] However, the two complementary $C_2C_1H_3$ and C_2C_1O bond angles are outside this range. The former was recently determined to be 129.1°,[14c] but calculations at all levels of theory predict it to be much smaller, ca. 122.6°. In view of the general computational experience[23] and the good theoretical–experimental agreement for the other structural parameters of **4a** we suggest that this experimental angle[14c] is too wide. A previous MW study,[14a,b] although less accurate than that in ref 14c, gave this angle as 123.9°. Furthermore, the complementary H_3C_1O bond angle is calculated to be 110.5° at MP2/6-31G**, a more reasonable value than the extremely small angle of 104.7° reported experimentally.[14c]

A poor agreement is found between the calculated and the experimental ordering of the C–H bond lengths. Thus, $r(C_1-H_3)$ > $r(C_2-H_2)$ > $r(C_2-H_1)$ (exp),[14c] $r(C_2-H_2)$ > $r(C_1-H_3)$ > $r(C_2-H_1)$ (MP2/6-31G**), and $r(C_1-H_3)$ = $r(C_2-H_1)$ > $r(C_2-H_2)$ (MP2/6-31G*). However, the differences are too small to allow a definitive ordering. Nevertheless, the difference in the theoretical and experimental orderings cast doubt on interpretations of these small bond length differences in terms of electronic effects.[14c,28]

The C–O bond length of 1.364 Å in **4a** is considerably shorter than that in MeOH (1.424 Å, both at MP2/6-31G*)[23] but longer than that in HC≡COH (1.325 Å, MP3/6-31G*).[29] This is ascribed to a change in carbon hybridization from sp³ in MeOH to sp² in **4a** and to sp in HC≡COH.[29] The C=C bond length in **4a** is almost identical with that in ethylene (1.336 Å at MP2/6-31G*).[23]

Analysis of experimental geometrical changes induced by alkyl substitution is yet impossible as **4a** is the only simple enol whose molecular structure is known experimentally with reasonable accuracy.[14] Theory is the only available reliable method for such

Table II. 3-21G Optimized Geometries of Enols **4b–g**

geometrical parameter[a]	$X_3 = C$				$X_3 = Si$	
	4b[b]	4c[c]	4d[d]	4e[e]	4f[f]	4g[g]
distance, Å						
$C_1=C_2$	1.317	1.317	1.317	1.318	1.318	1.319
C_1-X_3	1.500	1.502	1.505	1.515	1.910	1.927
C_1-O_4	1.381	1.381	1.381	1.385	1.391	1.392
O_4-H_5	0.966	0.965	0.965	0.965	0.970	0.968
X_3-R^1	1.080	1.082	1.083	1.536	1.474	1.906
X_3-R^2	1.084	1.084	1.542	1.545	1.474	1.915
X_3-R^3	1.084	1.541	1.542	1.545	1.474	1.915
C_2-H_6	1.069	1.069	1.069	1.067	1.070	1.071
C_2-H_7	1.074	1.074	1.074	1.074	1.076	1.076
angle, deg						
$C_1C_2H_6$	120.8	120.7	120.7	121.8	121.1	121.0
$C_1C_2H_7$	121.9	121.3	122.3	121.5	122.3	122.7
$H_6C_2H_7$	117.3	118.0	117.0	116.7	116.6	116.3
$X_3C_1C_2$	125.2	125.2	125.1	127.3	126.6	126.1
$O_4C_1C_2$	124.6	124.3	124.3	123.0	124.5	123.3
$O_4C_1X_3$	110.2	110.5	110.6	109.7	108.9	110.6
$R^1X_3C_1$	111.2	109.6	108.1	112.1	108.9	108.5
$H_5O_4C_1$	112.6	112.8	112.9	112.7	113.1	112.7
$R^1X_3C_1C_2$	0.0	4.1	0.0	0.0	0.0	180.0
$H_5O_4C_1C_2$	0.0	1.2	0.0	0.0	0.0	0.0

[a] For atom and group numbering see Figure 2b. [b] **4b**: $R^1 = R^2 = R^3$ = H. [c] **4c**: $R^1 = R^2$ = H; R^3 = Me. [d] **4d**: R^1 = H; $R^2 = R^3$ = Me. [e] **4e**: $R^1 = R^2 = R^3$ = Me. [f] **4f**: $R^1 = R^2 = R^3$ = H. [g] **4g**: $R^1 = R^2 = R^3$ = Me.
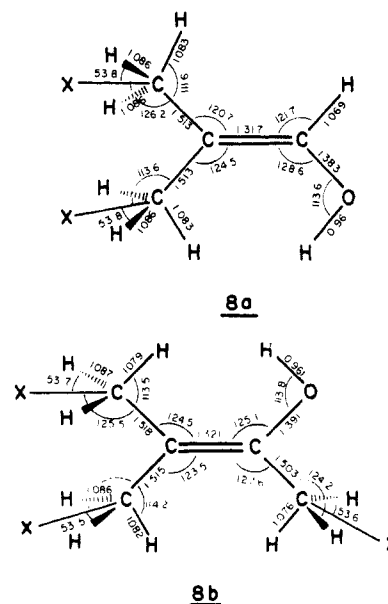

8a

8b

Figure 3. 3-21G optimized geometries of enols **8a** and **8b**.

(28) McKean, D. C. *Spectrochim. Acta* **1975**, *31A*, 1156.
(29) Stang, P. J.; Kitamura, T.; Karni, M.; Apeloig, Y. *J. Am. Chem. Soc.* **1990**, *112*, 374.

Table III. 3-21G Optimized Geometries of the Isomeric Enols 6Z and 6E

geometrical parameter[a]	6a (R = H)		6b (R = Me)		6c (R = Et)		6d (R = i-Pr)		6e (R = t-Bu)	
	Z	E	Z	E	Z	E	Z	E	Z	E
distance, Å										
$C_1=C_2$	1.315	1.313	1.318	1.317	1.318	1.318	1.318	1.318	1.319	1.321
C_1-O_4	1.379	1.381	1.383	1.389	1.383	1.389	1.383	1.389	1.385	1.392
C_1-R^3	1.072	1.070	1.501	1.500	1.502	1.502	1.506	1.506	1.529	1.528
C_2-C_7	1.510	1.509	1.510	1.508	1.513	1.508	1.513	1.509	1.514	1.510
angle, deg										
$R^3C_1C_2$	121.7	122.8	124.3	128.1	124.8	128.2	124.7	128.7	124.4	129.4
$R^3C_1O_4$	109.8	110.2	109.6	108.8	110.0	108.9	110.2	109.0	112.1	110.5
$O_4C_1C_2$	128.5	127.0	126.1	123.1	125.2	122.9	125.1	122.1	123.4	120.1
$C_7C_2C_1$	126.5	122.8	126.7	127.4	125.2	127.4	125.4	127.6	125.4	129.6
$H_6C_2C_1$	117.2	119.9	117.4	117.8	117.7	117.9	117.6	117.8	118.0	115.6
$H_5O_4C_1$	113.5	112.6	113.5	112.6	113.5	112.5	113.1	112.6	113.1	112.6
$H_8C_7C_2C_1$	0.0	0.0	0.0	0.0	0.0[b]	0.0[b]	0.0[b]	0.0[b]	0.0[b]	90[b]
$H_5O_4C_1C_2$	0.3	0.7	5.3	1.4	0.0	0.0	0.0	0.0	0.0	0.0

[a] For atom numbering see Figure 2c. [b] Not optimized.

analysis. For most enols geometry optimizations could be carried out only with 3-21G, but as this basis set reproduces quite well the geometry of **4a** and of other molecules[23] its use for analyzing substituent effects on enol geometries is justified. The most important structural parameters of the α-substituted enols **4** are collected in Table II and Figure 2b, structure **12**; those for the isomeric **6Z** and **6E** series in Table III and Figure 2c, and those for **8** and **9** in Figure 3. The following features are of interest:

(1) For all enols, the syn conformation around the C–O bond is the most stable. Steric repulsions between cis-methyl and hydroxy groups in enols **6Z** are too small to override this preference. However, they result in significantly smaller syn–anti energy differences (3-21G) in the **6Z** series (e.g., 1.2 kcal mol⁻¹ in **6Za**) than in the **6E** series (e.g., 2.8 kcal mol⁻¹ in **6Ea**) or in the **4** series (e.g., 3.0 kcal mol⁻¹ in **4a**). Previous calculations show that enols $H_2C=C(OH)X$ and $XCH=CHOH$ (X = Li, BeH, BH_2, CH_3, NH_2, OH, F),[20a] **6Zb**,[9] and **8**[9] also adopt the syn conformation. Even the congested enols **3** have syn conformations in poor hydrogen bond accepting solvents[16] and in the solid state,[17] although an intramolecular $\pi(\beta'-Mes)$–HO hydrogen bond stabilizes this conformation.[16] Anti conformations are observed where the enolic OH is intramolecularly hydrogen bonded to EtOH of crystallization.[17b] The calculations predict for **6Za** and **8a** a predominant syn conformation in the gas phase while in slightly aqueous acetone they exist predominantly in the anti conformation.[15] Apparently, the relatively small syn–anti energy difference is overcome by a more effective solvation of the anti conformation.

(2) In the most stable conformation of **4b–d** a β'-hydrogen of the α-alkyl group eclipses the C=C bond as shown in **12** (R¹ = H; Figure 2b), in analogy with propene.[13c] In **4e** the rotational barrier of the tert-butyl group is nearly zero, and in the preferred conformation the C=CCC(H_3) dihedral angles are 90°, 210°, and 330°. The geometry changes along the series **4b** to **4e** are generally small, e.g., the $C_1=C_2$ bond lengthens by only 0.001 Å and the $O_4C_1X_3$ ($X_3=C$) bond angle (Figure 2b) widens by only 1.6° when R changes from Me to the bulky t-Bu. The geometrical changes are somewhat larger upon substitution of hydrogen by methyl (Table II). The only significant geometrical changes between **4b** and **4e**, probably reflecting minimalization of steric repulsions involving the bulky tert-butyl group, are the 0.015 Å lengthening of the C_1X_3($X_3=C$) bond, the 2.1° widening of the $C_2C_1X_3$ angle, and the shrinking of the $C_2C_1O_4$ angle by 1.6°. The C–Si bond distances of 1.910 and 1.927 Å in the α-silyl enols **4f** and **4g** are significantly longer than those in vinylsilane (1.852 Å, 3-21G).

(3) Scheme I gives the relative energies of some important conformations of **6Za**, **6Ea**, **6Zb**, and **6Eb**. In spite of the presence of the β-methyl group, all adopt a syn conformation. In the **6Z** series the β-methyl group adopts the eclipsing conformation and the α-R substituent adopts the same conformation as in the corresponding **4** series. Rotation of the β-methyl group in the Z isomers from its syn conformations (e.g. **13Z**) to a staggered conformation (e.g., **14Z**) requires relatively little energy, e.g., 0.6

Table IV. Calculated Relative Energies (kcal mol⁻¹) at Various Levels of Theory of Vinyl Alcohol (**4a**) and Acetaldehyde (**5a**) and of Propen-2-ol (**4b**) and Acetone (**5b**)

method	ΔE(4a–5a)	ΔE(4b–5b)[a]
3-21G//3-21G	8.5	11.2
6-31G*//3-21G	16.2	19.0
6-31G*//6-31G*	17.0	18.8
6-31G**//6-31G*	14.8	
6-31G**//6-31G**	13.5	
MP2/6-31G*//3-21G	17.3	19.0
MP2/6-31G*//6-31G*	16.5	18.3
MP3/6-31G*//6-31G*	14.7	16.7
MP4SDTQ/6-31G*//6-31G*	16.8	
MP4SDTQ/6-31G**/6-31G**	14.4	
MP2/6-31G*//MP2/6-31G*	16.8	
zero-point energy	0.54	0.23
ΔS°[b]	-1.70	-3.69[b,c]

[a] Total energies are given in the supplementary material. [b] cal K⁻¹ mol⁻¹. [c] ΔS° = -3.5 ± 1.5 cal⁻¹ K⁻¹ mol⁻¹ in water and -7.4 ± 1.9 cal K⁻¹ mol⁻¹ in acetonitrile.[37]
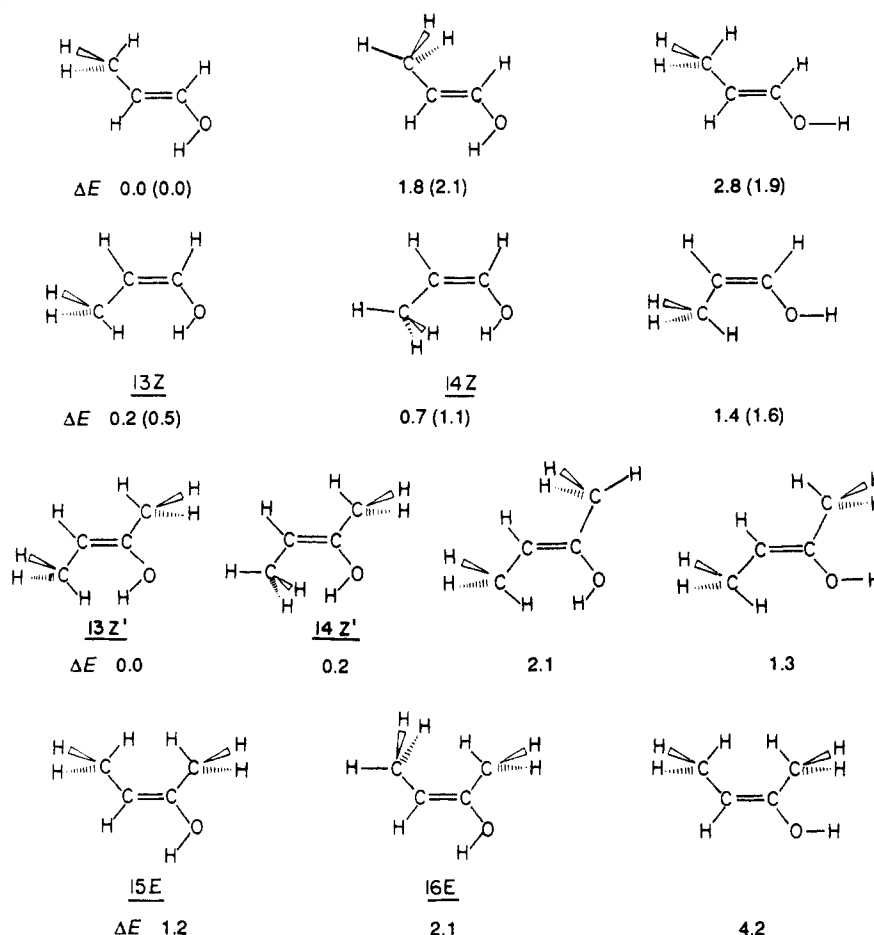
Table V. Calculated Relative Energies (kcal mol⁻¹) of Enol **4** and of the Corresponding Carbonyl Compounds **5**

substituent R	ΔE(4–5)		substituent R	ΔE(4–5)	
	3-21G	6-31G*		3-21G	6-31G*
H	8.5	16.2	t-Bu	10.8	
Me	11.2	19.0	SiH₃	3.2	12.9[a]
Et	12.2	20.1	SiMe₃	5.3	
i-Pr	10.8	18.9			

[a] 12.4 and 12.1 kcal mol⁻¹ at 6-31G*//6-31G*.

kcal mol⁻¹ in **6Za** (6-31G*//3-21G) and 0.2 kcal mol⁻¹ in **6Zb** (i.e., **13Z'–14Z'**). The corresponding energy differences in **6Ea** and in propene are significantly larger, 2.1 kcal mol⁻¹, respectively, at 6-31G*//3-21G. Structure **15E**, in which β-Me and α-R hydrogens simultaneously eclipse the double bond, is the most stable conformation also in **6Ea** and **6Eb**. However, conformation **16E** in which the β-Me staggers the C=C bond is only 0.9 kcal mol⁻¹ higher in energy.

(4) The geometries of **4a** and **6Za** or **6Ea** (Tables II and III and Figure 2b,c) are similar, except that in **6** the C=C and C—O bonds are 0.002–0.003 Å longer. The C=C and C—O bonds are elongated by 0.003–0.006 Å on replacing the α-hydrogen in **4** and **6** by methyl. In the **6E** isomers the C–O bond distances are generally (except for **6Za–6Ea**) longer (by ca. 0.006 Å), the $R^3C_1C_2$ bond angles are wider (by ca. 4°), and the $O_4C_1C_2$ bond angles are smaller (by ca. 3°) than in the corresponding **6Z** isomers. We attribute these changes to a larger steric congestion between R^3 and the β-Me in **6E** than that between the cis-OH and Me in **6Z**. This is most pronounced in **6Ee**, especially in the elongated C–O bond (1.392 Å) and the wide $R^3C_1C_2$ and $C_7C_2C_1$ bond angles (129.4–129.6°). Larger changes in these bond angles are observed in the more congested **3c–f**.[17b]

Scheme I. Relative Energies (kcal mol⁻¹) at 3-21G of Several Conformations of **6Za** and **6Ea** and of **6Zb** and **6Eb**[a]

ΔE 0.0 (0.0)   1.8 (2.1)   2.8 (1.9)

13Z   **14Z**

ΔE 0.2 (0.5)   0.7 (1.1)   1.4 (1.6)

13 Z'   **14 Z'**

ΔE 0.0   0.2   2.1   1.3

15E   **16E**

ΔE 1.2   2.1   4.2

[a] Values in parentheses are at 6-31G*//3-21G.

Table VI. Calculated Relative Energies (kcal mol⁻¹) of **6Z**, **6E**, and **7**[a,b]

R	$\Delta E(6E-6Z)$	$\Delta E(6-7)$		$\Delta\Delta E(\beta\text{-}CH_3)$[c]	
		Z	E	Z	E
H	-0.2 [1.2][d]	9.7 [4.3][d]	9.5 [5.5][d]	1.2	1.0
	(-0.5)	(17.2)[e]	(16.7)	(1.0)	(0.5)
Me	1.20 [0.5][d]	12.6 [6.4][d]	13.8 [6.9][d]	1.4	2.6
		(20.2)		(1.2)	
Et	1.2	13.5	14.7	1.3	2.5
i-Pr	1.5	12.2	13.7	1.5	3.0
t-Bu	4.8	15.2	20.1	4.4	9.3

[a] Total energies are given in the supplementary material. [b] At 3-21G//3-21G. Values in parentheses are at 6-31G*//3-21G. [c] $\Delta\Delta E$-(β-CH₃) = $\Delta E(6-7)$ - $\Delta E(4-5)$. [d] Experimental value in the gas phase.[9] [e] 13.4 kcal mol⁻¹ at 6-31G**//3-21G.

B. Relative Energies of the Carbonyl and Enol Tautomers. The calculated energy differences (mostly at both 3-21G//3-21G and 6-31G*//3-21G) between the carbonyl and the enol tautomers (ΔE) are given for the **4a-5a** and **4b-5b** pairs in Table IV, for the other **4-5** pairs in Table V, and for the **6-7** pairs in Table VI. As expected, the carbonyl form is always substantially more stable than the enol form (i.e., positive ΔE(enol-carbonyl) values). However, there are large differences between the 3-21G//3-21G and the 6-31G*//3-21G estimates of ΔE(enol-carbonyl), the latter being higher by ca. 8 kcal mol⁻¹. Surprisingly, the limited available experimental data are in better agreement with the generally inferior[23] 3-21G values. The effect of the level of theory on ΔE was probed in more detail for the parent **4a-5a** and **4b-5b** pairs, and the computational results were compared with experiment.

1. The Vinyl Alcohol-Acetaldehyde and the Propen-2-ol-Acetone Pairs. a. Gas Phase. The comparison of enols with the isomeric carbonyls is non-isodesmic, and relatively large changes

in ΔE as a function of the theoretical method are therefore expected.[23] It is of interest to study these changes for the smaller systems. For the **4a-5a** and **4b-5b** pairs we find that geometry optimizations with basis sets more extended than 3-21G or the addition of correlation energy has a small effect of only ca. 1-2 kcal mol⁻¹ on ΔE(enol-keto) (cf. Table IV). Thus, ΔE(**4a-5a**) values are 16.8 and 16.2 kcal mol⁻¹ at MP4SDTQ/6-31G*//6-31G* and 6-31G*//3-21G, respectively. Geometry optimizations at a correlated level also have a small effect and ΔE(**4a-5a**) = 16.8 and 16.5 kcal mol⁻¹ at MP2/6-31G*//MP2/6-31G* and MP2/6-31G*//6-31G*, respectively. Surprisingly, addition of polarization functions *on hydrogen* reduces ΔE(**4a-5a**) significantly. At 6-31G**//6-31G* ΔE(**4a-5a**) = 14.8 compared with 17.0 kcal mol⁻¹ at 6-31G*//6-31G*. Geometry optimizations at 6-31G** reduce ΔE(**4a-5a**) to 13.5 kcal mol⁻¹, mostly by affecting the enol.

In two papers[30] published after this work was completed, it was found that further splitting of the valence shell and the addition of diffuse functions (the latter probably has a small effect[21a]) reduces further the enol-aldehyde energy difference. Thus, ΔE-(**4a-5a**) = 12.4 kcal mol⁻¹ at 6-311++G**//6-31G*,[30a] 12.9 kcal mol⁻¹ at MP4/6-311+G**//6-31+G*,[30b] and 11.9 and 10.4 kcal mol⁻¹ at MP2 and MP3/6-311++G**//6-31G*,[30a] respectively. Note that the MP4 and MP2 ΔE values are similar (Table IV). Thus, the best current theoretical estimate of ΔE(**4a-5a**) is 11.9 (MP2/6-311++G**//6-31G*), -1.3 (estimated effect of optimization at 6-31G**, see Table IV), and +0.5(ZPE) = 11.1 kcal mol⁻¹. It is interesting that the 3-21G//3-21G ΔE values are much closer to these best estimates than the 6-31G* values. Similarly, the best theoretical estimated ΔE(**4b-5b**) (at 0 K) is ca. 14 kcal

(30) (a) Wiberg, K. B.; Breneman, C. M.; LePage, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 61. (b) Smith, B. J.; Radom, L.; Kresge, A. J. *Ibid.* **1989**, *111*, 8297.

mol^{-1}. Comparisons with experimental data require corrections for changes of ΔH_f from 0 to 298 K, but these contribute at most a fraction of a kcal mol^{-1}.[31]

The calculations apply strictly only to the gas phase, where relevant experimental gas-phase data are available only for a few aldehydes and ketones.[9,11,12] On the basis of simple additivity, Holmes et al. *estimated* that acetaldehyde **5a** is more stable than vinyl alcohol **4a** by 13.2 kcal mol^{-1},[11a] but they later used measured ionization energies to deduce that **5a** is more stable than **4a** by 9.9 ± 2.0 kcal mol^{-1} and that acetone **5b** is more stable than **4b** by 13.9 ± 2.0 kcal mol^{-1}.[11b] Tureček and Havlas first reported significantly smaller differences, i.e., $\Delta E(\textbf{4a–5a}) = 9.1$ kcal mol^{-1} and $\Delta E(\textbf{4b–5b}) = 10.0$ kcal mol^{-1},[12a] but more recently they corrected $\Delta E(\textbf{4b–5b})$ to 11.2 kcal mol^{-1}.[9] An older report gave $\Delta G°(\textbf{4b–5b}) = 13.9 \pm 2$ kcal mol^{-1}.[12b] Gas-phase ΔE(enol-keto) values of other alkyl-substituted keto-enol pairs are around 10 kcal mol^{-1} or even lower.[12a] Our best calculated $\Delta E(\textbf{4a–5a})$ and $\Delta E(\textbf{4b–5b})$ values are slightly higher, 11 and 14 kcal mol^{-1}, respectively.[30,32]

An unequivocal decision as to whether the small discrepancy of 2–3 kcal mol^{-1} between the recent experimental $\Delta H_f(\textbf{4a–5a})$ and $\Delta H_f(\textbf{4b–5b})$ values and our calculated values is due to the calculations, to the experiment, or to both is difficult. However, it should be noted that the gas-phase energy differences are not very accurate as they were not determined by direct measurements of the keto-enol equilibria, and as the ΔH_f of the enols were not corrected for temperature effects. More accurate experimental measurements as well as more sophisticated calculations of the **4a–5a** and **4b–5b** energy differences are required to establish more accurately these fundamental values.

b. Solution. Most of the experimental K_{enol} values are in water.[1c,4] Comparison of the derived keto-enol ΔG values with the calculated gas-phase enthalpy differences requires knowledge of the entropy contributions. The calculations (Table IV) show that keto-enol isomers have similar entropies, in agreement with experimental data. At 298 K, the $T\Delta S$ term favors the C=O form by only 0.5 and 1.1 kcal mol^{-1} for the **4a–5a** and **4b–5b** pairs, respectively.

Solvation may affect the keto-enol equilibria, but directly measured data were unavailable when this work was conducted. Since the experimental $\Delta E(\textbf{4a–5a})$ and $\Delta E(\textbf{4b–5b})$ values are almost identical in the gas phase[9,11,12] and in aqueous solution,[1c,4] it might be concluded that there is no significant differential solvation of one of the tautomers. However, if the higher calculated gas-phase ΔE values are correct (see above), then the K_{enol}(water) are larger by 2–3 kcal mol^{-1} than in the gas phase, suggesting a somewhat better solvation in water of the enol than of the carbonyl form. The data below support the latter conclusion.

A group additivity scheme for calculating $\Delta G_s(H_2O)$ values was suggested,[33a] but the data are insufficient to enable such calculations for most of the enol-carbonyl pairs of interest. $\Delta G_f(H_2O, 25$ °C) values of −24.38 and −32.88 kcal mol^{-1} were calculated for $CH_2=CHOH$ and CH_3CHO, respectively.[33b]

The solvent effect could be estimated from the free energies of solution (ΔG_s) of the two species, using data kindly provided by Professor M. H. Abraham. The relevant $\Delta G_s(H_2O)$ values (standard state: 1 atm gas; unit mole fraction in water) at 298 K are the following: 0.77 (**5a**), 0.46 (**5b**), 0.56 (**5c**), 1.03 (**5d**), 1.53 (**5e**),[33d] 0.83 (**7a**), 0.56 (**7b**), 0.86 (**7c**), 1.21 (**7d**),[33e] 1.66 (**7e**) (est.), 1.41 (**9**) kcal mol^{-1},[33c] showing that all carbonyls are destabilized on transfer to water, the more so the bulkier the species. ΔG_s values for enols are unavailable. However, comparison of ΔG_s for $CH_2=CHCH_2X$ and $CH_3CH_2CH_2X$ (X = OH, Cl, Br) shows that an allylic double bond enhances solvation by 0.24 ± 0.05 kcal

mol^{-1}.[33c] Using this value for the contribution of a *vinylic* double bond, together with ΔG_s's of the corresponding saturated alcohols,[33c] gives the following ΔG_s(enol) values: −0.97 (**4a**), −0.72 (**4b**), −0.59 (**4c**), −0.39 (**4d**), −0.20 (**4e**) (extrapolated), −0.82 (**6a**), −0.59 (**6b**), −0.36 (**6c**), 0.14 (**6d**), 0.37 (extrapolated) (**6e**), −0.47 (**8a**) kcal mol^{-1}.[33c] Hence, the enols are stabilized by transfer to water except for the bulkier **4d** and **4e**. Consequently, the estimated *increased stabilities* of enols relative to the carbonyl isomers on transfer from gas phase to water are −1.74 (**4a**), −1.18 (**4b**), −1.15 (**4c**), −1.42 (**4d**), −1.73 (**4e**), −1.65 (**6a**), −1.15 (**6b**), −1.22 (**6c**), −1.07 (**6d**), −1.29 (**6e**), −1.88 (**8a**); i.e., in water ΔE(enol–carbonyl) decreases (K_{enol} increases) by 1–2 kcal mol^{-1} relative to the gas phase. The differential effect of α-alkyl or β-methyl groups is small.

The scarce available data on the solvent dependence of K_{enol} values are consistent with the conclusions above. For the simplest (yet bulkier than **4**, **6**, or **8**) enols where data are available, K_{enol} increased (ΔE(enol–keto) decreased) with the solvent polarity (π^*) and hydrogen bond accepting ability (β) parameters of the Kamlet–Taft solvatochromic equation.[34] Thus, K_{enol} of p-$O_2NC_6H_4C(Me)=CHOH$ is 1.5 in DMSO ($\pi^* = 1.00$, $\beta = 0.76$[34]) but only the ketone is observed (i.e., $K_{enol} < 0.02$) in CCl_4 ($\pi^* = 0.29$, $\beta = 0$[34]) or benzene ($\pi^* = 0.59$, $\beta = 0$[34]).[8a] For 2-(2,4,6-triisopropylphenyl)acenaphthyl enol $K_{enol} = 2.6$ in DMSO and ≤ 0.004 in hexane ($\pi^* = 0.04$, $\beta = 0$[34]); i.e., solvation by DMSO stabilizes the enol by >3.8 kcal mol^{-1} [35a] Likewise, for $Ph_2C=C(OH)H$ $K_{enol}(DMSO)/K_{enol}(H_2O) = 45$.[8c,35b] For K_{enol} of 5,5-dimethyl-1,3-cyclohexanedione, the β term of the solvent is overwhelmingly more significant than the π^* or the solvent hydrogen bond donating ability (α) terms.[36] Similar results apply for enols **3**.[16] Since $\beta(H_2O) = 0.14$ is closer to β(hexane) than to β(DMSO), K_{enol} values should change only slightly between the gas phase and water, in qualitative agreement with the conclusion above.

In a paper published shortly before our work was submitted for publication Kresge et al.[37] investigated the **4b** ⇌ **5b** tautomerization in H_2O and MeCN ($\pi^* = 0.75$, $\alpha = 0.19$, $\beta = 0.31$[34]). The enol was found to be slightly more favored in the equilibrium in MeCN ($pK_{enol} = 7.96 \pm 0.02$, $\Delta H° = 8.7 \pm 0.6$ kcal mol^{-1}, $\Delta S° = -7.4 \pm 1.9$ cal K^{-1} mol^{-1}) than in water ($pK_{enol} = 8.33 \pm 0.02$, $\Delta H° = 10.30 \pm 0.4$ kcal mol^{-1}, $\Delta S° = -3.5 \pm 1.5$ cal K^{-1} mol^{-1}). Both K_{enol} values are higher in solution than in the gas phase. Kresge et al. regarded these $\Delta H°$ values in solution as being "close" to the *average* gas-phase $\Delta H°$ value of 12 ± 2 kcal mol^{-1} and concluded that "the heats of solvation of the keto and the enol forms of acetone in water are quite similar and that the corresponding values for acetonitrile solution are not very different as well". However, the two gas-phase $\Delta H°$ values used in the averaging differ sufficiently so that a choice of one of them can profoundly change this conclusion.

We conclude from the limited data that K_{enol} values of simple enols are somewhat larger in water than in the gas phase. This brings the calculated gas-phase K_{enol} values to a close agreement with the experimental K_{enol} values in solution. This conclusion about the solvent effect on K_{enol} is less consistent with the *experimental* gas-phase K_{enol} values, supporting our belief (see above) that these values are by 2–3 kcal mol^{-1} too low. Additional measurements and calculations[38] of $\Delta H_s°$ values of simple keto-

(31) See for example ref 23, pp 258–260.

(32) A recent theoretical analysis of Brønsted acidities concluded that $\Delta E(\textbf{4b–5b})$ is even smaller, i.e., only 7–9 kcal mol^{-1}.[21a]

(33) (a) Hine, J.; Mookerjee, P. K. *J. Org. Chem.* **1975**, *40*, 292. (b) Harcourt, M. P.; More O'Ferrall, R. A. *Bull. Soc. Chim. Fr.* **1988**, 407. (c) Abraham, M. H.; Whiting, G. S.; Fuchs, R.; Chambers, E. S. *J. Chem. Soc., Perkin Trans. 2* **1990**, 291. (d) Cabani, S.; Gianni, P.; Mollica, V.; Lejori, L. *J. Soln. Chem.* **1981**, *10*, 563. (e) Value for 4-methylpentan-2-ol.

(34) (a) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 485. (b) For a list of recent β values, see: Kamlet, M. J.; Doherty, R. M.; Abraham, M. H.; Carr, P. W.; Doherty, R. F.; Taft, R. W. *J. Phys. Chem.* **1987**, *91*, 1966. (c) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH: Weinheim, 1988; See table on p 378.

(35) (a) Miller, A. R. *J. Org. Chem.* **1976**, *41*, 3599. (b) Rochlin, E.; Rappoport, Z. Unpublished results.

(36) Mills, S. G.; Beak, P. *J. Org. Chem.* **1985**, *50*, 1216.

(37) Chiang, Y.; Kresge, A. J.; Schepp, N. P. *J. Am. Chem. Soc.* **1989**, *111*, 3977.

(38) (a) Simple solvation calculations based on bulk solvent effects are reported in ref 20c,f. (b) For more sophisticated calculations of the solvation energies of the pyridone–pyridol isomers and similar compounds see: Cieplak, P.; Bash, P.; Singh, U. C.; Kollman, P. A. *J. Am. Chem. Soc.* **1987**, *109*, 6283. Cieplak, P.; Geller, M. *J. Mol. Struct.* **1989**, *184*, 221. (c) For a general review see: Jorgensen, W. L. *Acc. Chem. Res.* **1989**, *22*, 184.
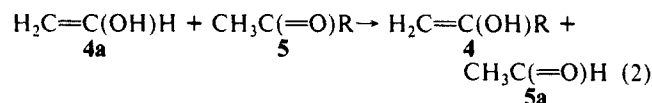
Table VII. Calculated Energies for Equations 2–5[a,b]

substituent R	eq 2[c]	eq 3	eq 4	eq 5
H	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
Me	2.7 (2.8)	6.6 (6.3)	9.3 (9.2)	2.8 (2.4)
Et	3.7 (3.9)	7.0 (5.8)	11.1 (9.6)	3.6 (2.1)
i-Pr	2.3 (2.7)	8.0 (5.3)	10.3 (8.0)	4.3 (1.8)
t-Bu	2.3	6.8	9.2	4.3
SiH$_3$	–5.3 (–3.3)	1.4 (–0.2)	–3.8 (–3.4)	–0.7
SiMe$_3$	–3.2	2.0	–1.1	0.3

[a] All values in kcal mol^{-1}. [b] At 3-21G//3-21G. Values in parentheses are at 6-31G*//3-21G. [c] These values denote the α-alkyl-substituent effect, i.e., $\Delta\Delta E = \Delta E(4$–$5) - \Delta E(4a$–$5a)$.

enol pairs are required to resolve this question.

2. Alkyl-Substituent Effects on the Carbonyl-Enol Energy Difference. The major theoretical difficulty in evaluating the relative energies of **4** and **5** is that this comparison is non-isodesmic,[23,39] i.e., the two molecules contain different types of bonds (C—C, C=O, and C—H in **5** and C=C, C—O, and O—H in **4**). Such comparisons are frequently very sensitive to the quality of the basis set and to electron correlation effects.[23] In contrast, isodesmic equations are usually relatively insensitive to the computational method and frequently give energies within 1 kcal mol^{-1} of the experimental values, even at 6-31G*//3-21G.[23] Fortunately, substituent effects on the enol–keto energy difference can be calculated by isodesmic comparisons, e.g., eq 2 for evaluating $\Delta E(4$–$5)$, and it is therefore expected that substituent effects will be reproduced quite accurately with either 6-31G*//3-21G or 3-21G//3-21G.

$$\text{H}_2\text{C}=\text{C(OH)H} + \text{CH}_3\text{C(=O)R} \rightarrow \text{H}_2\text{C}=\text{C(OH)R} +$$
$$\textbf{4a} \qquad\qquad \textbf{5} \qquad\qquad\qquad \textbf{4}$$
$$\text{CH}_3\text{C(=O)H} \quad (2)$$
$$\textbf{5a}$$

The advantage of isodesmic comparisons is demonstrated by comparing the directly calculated ΔE(enol–carbonyl), which are very different at 3-21G and 6-31G* (Table V), with the calculated substituent effects (eq 2), which are very similar at the two computational levels (Table VII). The following conclusions emerge from the calculations:
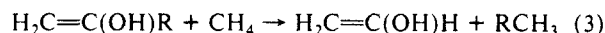
a. The Effect of an α-Alkyl Group on $\Delta E(4$–$5)$. Substitution of hydrogen by an α-alkyl group R increases $\Delta E(4$–$5)$ (Table V). This effect (eq 2, Table VII) is alkyl group dependent and does not change monotonously with the bulk of R, in contrast to K_{enol} of **3b–f**.[5a,7a] ΔE(enol–carbonyl) increases (6-31G*//3-21G) for the changes R = H → Me (by 2.8 kcal mol^{-1}) and R = Me → Et (by an additional 1.1 kcal mol^{-1}), decreases for R = Et → *i*-Pr (by 1.2 kcal mol^{-1}), and is practically the same for R = *i*-Pr and R = *t*-Bu (Table VI). Thus, the calculated $\Delta E(4$–$5)$ values are constant, within 1.5 kcal mol^{-1}, along the series R = Me, Et, *i*-Pr, *t*-Bu, and ΔE is only 0.4 kcal mol^{-1} lower for R = *t*-Bu than for R = Me.

In the gas phase ΔE(enol–carbonyl) values are available only for the **4a–5a** and **4b–5b** pairs, but the experimental determinations of the methyl substituent effect differ appreciably, emphasizing the significant inaccuracies in these values.[1e] Holmes and Lossing[11c] reported a methyl effect of 4.0 kcal mol^{-1}, Lifshitz et al.[12d] reported 2.15 kcal mol^{-1}, while Tureček et al.[12a] first reported 0.9 kcal mol^{-1} and more recently corrected it, by using Lifshitz's ionization energy, to 2.0 kcal mol^{-1}.[9] The calculations predict (at MP3/6-31G*//6-31G*) a methyl effect of 2.0 kcal mol^{-1} (Table IV), supporting the value of Lifshitz et al.[12d]

The recent experimental K_{enol}(**4**–**5**) values in water[4] overall agree with the computations. Thus, Kresge et al. also find an almost constant $\Delta G(4$–$5)$ for R = Me, Et, *i*-Pr, *t*-Bu.[4c] As in the calculations, ΔE in water increases in the order Et > Me > H and

(39) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

(40) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 93.

the corresponding substituent effects for the changes R = H → Me, Me → Et, Et → *i*-Pr, and *i*-Pr → *t*-Bu are (kcal mol^{-1}, calculated 6-31G*//3-21G values in parentheses) the following: 2.6 (2.8), 0.53 (1.1), –0.15 (–1.2), 0.15 (0.1, 3-21G), respectively.[4c] The experimental–computational agreement shows that for the **4–5** series water has only a small differential solvation effect on K_{enol}. This points to similar differential alkyl-substituent effects on the ΔH_s° values of each enol–ketone pair, in agreement with recent values of Abraham.[33c]

We have separated the total effect of R to contributions from the enols (eq 3) and from the ketones (eq 4). Substraction of eq 3 from eq 4 yields eq 2.

$$\text{H}_2\text{C}=\text{C(OH)R} + \text{CH}_4 \rightarrow \text{H}_2\text{C}=\text{C(OH)H} + \text{RCH}_3 \quad (3)$$

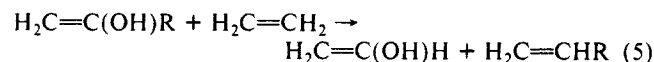$$\text{RC(=O)CH}_3 + \text{CH}_4 \rightarrow \text{HC(=O)CH}_3 + \text{RCH}_3 \quad (4)$$

The 3-21G values (for which data are available for all substituents) in Table VII show that alkyl substituents stabilize significantly both the ketones and the enols. The stabilization is larger for the ketones with a consequent increase in ΔE for alkyl relative to hydrogen substitution. The stabilizing interactions between R and the C=O group (eq 4) reach a maximum of 11.1 kcal mol^{-1} for R = Et and then decrease to 10.3 and 9.2 kcal mol^{-1} for R = *i*-Pr and *t*-Bu, respectively. We ascribe this change to the fact that when methyl replaces ethyl in **5** the C—H/C=O eclipsing interaction is replaced by a more stabilizing C—C/C=O arrangement. Thus, rotation around the C–C bond in 2-butanone from **17A** (most stable conformation) to **17B** (with eclipsing C—H and C=O) raises the energy by 2.7 kcal mol^{-1}. Substituting the β-hydrogen of the α-ethyl group in **17A** by methyls decreases the stabilizing effect by R, despite the favorable inductive effect, due to steric crowding which is the largest for R = *t*-Bu. The delicate balance of effects results in practically identical overall stabilization of **5** when R = Me or *t*-Bu (Table VII).
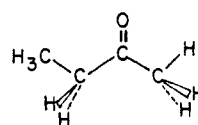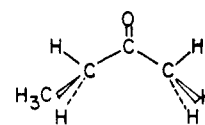
17A **17B**

A similar trend is found for alkyl effects in the enols (eq 3), with the maximal stabilization of 8.0 kcal mol^{-1} for R = *i*-Pr. In **4e** a methyl group replaces the hydrogen which eclipses the C=C bond in **4b–d**. The increase in steric congestion, revealed by the geometry (Table II), reduces the stabilizing effect of R to 6.8 kcal mol^{-1}.

Equation 5 is endothermic for all R groups (Table VII), and the order of geminal stabilization between R and the OH groups is *t*-Bu = *i*-Pr > Et > Me. The energies of eq 5 are ca. half of the corresponding energies of eq 3, showing that a major stabilizing factor in the latter comparison is the transfer of R from a sp^2 carbon in **4** to a sp^3 carbon in CH$_3$R. The same factor contributes to the relatively large stabilization energies of the ketones (eq 4).

$$\text{H}_2\text{C}=\text{C(OH)R} + \text{H}_2\text{C}=\text{CH}_2 \rightarrow$$
$$\text{H}_2\text{C}=\text{C(OH)H} + \text{H}_2\text{C}=\text{CHR} \quad (5)$$

b. The Effect of an α-Silyl Group.[18d] Silicon is more electropositive than carbon,[40] and formal analogy with the effect of alkyl groups suggests that a silyl substituent should increase ΔE(enol–carbonyl). A carbenium ion can be regarded as a model for a carbonyl group due to its dipolar hybrid structure R$_2$C$^+$–O$^-$. Since we found computationally and experimentally that relative to a methyl an α-silyl substituent destabilizes carbenium ions,[18a–c] we hypothesized that α-silyl ketones, such as **5f** and **5g**, would be destabilized relative to analogous α-alkyl ketones, i.e., α-silyl substitution should reduce ΔE(enol–keto). This conclusion is substantiated by calculations. At 6-31G*//3-21G $\Delta E(\textbf{4f}$–$\textbf{5f})$ is only 12.9 kcal mol^{-1} (12.1 at MP2/6-31G*//6-31G*), 6.1 kcal mol^{-1} lower than $\Delta E(\textbf{4b}$–$\textbf{5b})$, which amounts to a ca. 25000-fold increase in K_{enol} at 25 °C. The effect of the Me$_3$Si group is similar

Table VIII. Calculated and Experimental β-Methyl Effects (kcal mol^{-1}) on ΔE(enol–carbonyl)[a]

method	4a	6Za	6Ea	8a	4b	6Zb	6Eb	8b
calculated[b]	0	−0.5 (1.0)	−0.7 (0.5)	1.2 (−0.6)	0	1.4 (1.2)	2.6	0.8
experimental								
gas phase[9]	0	−4.8	−3.6	−6.9	0[d]	−3.3[d]	−4.3[d]	−6.2[d]
water[4d]	0	c	c	−3.2	0	−1.1[e]	−1.1[e]	−1.3

[a] The values given are the differences between the ΔE values of two pairs of carbonyl–enol tautomers, e.g., the ΔE values for **8b** are ΔE(**8b–5b**) − ΔE(**4b–5b**). A negative sign indicates that β-methyl substitution decreases the keto–enol energy difference. [b] At 3-21G//3-21G, values in parentheses are at 6-31G*//3-21G. [c] Not available. [d] Using a ΔE(**4b–5b**) value of 11.2 kcal mol^{-1}.[9] [e] Stereochemistry of the enol was not determined.

**Table IX.** Calculated Energies (kcal mol^{-1}) of Equations 6, 7, 11, 13, and 14[a]

substituent R	eq 6		eq 7	eq 11	eq 13		eq 14	
	6Z	6E		6Z	6Z	6E	6Z	6E
H	2.2 [8.7][b] (1.8)	2.4 [7.5][b,d] (2.3)	1.7 [2.4][c] (2.8)	−1.5 (−2.2)	0.0	0.0	0.0	0.0
Me	1.8 [8.3][b]	0.6 [7.8][b,d] (0.3)	3.2 [2.9][c] (1.5)	−1.9 (−2.7)	6.2 (5.8)	5.0	2.4 (1.8)	1.0
Et	1.7	0.5	3.0 [2.3][c]	−2.0	6.8	5.6	3.1	1.6
i-Pr	1.8	0.3	3.2 [3.4][c]	−1.9	7.6	6.1	3.9	3.7
t-Bu	−1.7	−6.5	2.7 [3.2][c]	−5.4	2.9	−1.9	0.5	−4.5

[a] At 3-21G//3-21G. Values in parentheses are at 6-31G*//3-21G. [b] Experimental values, using heats of formation of the enols from ref 9 and ΔH_f = −17.8 and −20.0 kcal mol^{-1} for CH_4 and C_2H_6, respectively. [c] Experimental values, using thermochemical data from ref 42. [d] Uncorrected to zero-point vibrational energy and to 0 K.

(Table VII). As predicted, the reduction of ΔE is mainly due to the destabilizing effect of an α-silyl group in the ketone (by 3.8 kcal mol^{-1} at 3-21G), while a methyl group is stabilizing by 9.3 kcal mol^{-1} (eq 4). The complementary stabilization by α-SiH$_3$ in the enols (eq 3, 1.4 kcal mol^{-1}) is significantly smaller than that of α-Me (6.6 kcal mol^{-1}), also contributing to reduction of ΔE by α-silyl substitution.

These theoretical predictions were confirmed experimentally. Equilibration studies in hexane showed that K_{enol} values for **3h**, **3c**, and **3f** are >20, 0.64, and 0.06, respectively.[18d] A direct confirmation is Kresge and Tobin's recent finding that in water pK_{enol} of MeCOSiMe$_3$ is 4.88, 3.45 pK units (i.e., ΔE = 4.7 kcal mol^{-1}) lower than for acetone.[41]

c. The β-Methyl-Substituent Effect. Between isomers **6Z** (with cis-β-Me and -OH substituents) and **6E** (with trans-Me and -OH), **6Z** is generally calculated to be more stable, except for **6a** where the E isomer is lower in energy by 0.2 kcal mol^{-1} (Table VI). As expected ΔE(**6E–6Z**) increases with the steric bulk of α-R and is largest (4.8 kcal mol^{-1}) for R = t-Bu. Similarly, **18E** is more stable than **18Z** by 3.9 kcal mol^{-1}.[42] Thus, except for **6a**, **6Z** will be the major enol component in equilibrium with the ketone **7**. For example, in the **7b–6b** equilibrium the calculated enol fraction consists of **6Zb** and **6Eb** in a 88:12 ratio at 298 K. The available experimental data for **6a** and **6b** (Table VI) are consistent with the calculations, considering the experimental errors and the assumption that the cation radicals derived from the E and Z isomers have identical $\Delta H_f°$ values.[9]
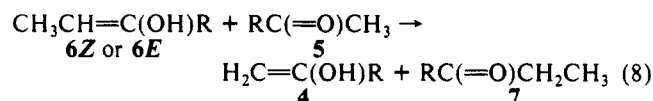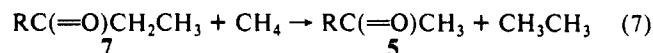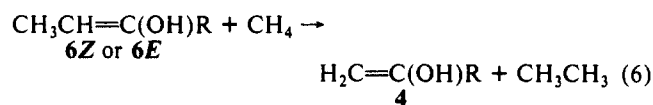

18E   **18Z**
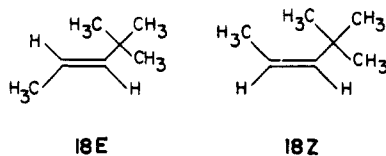
The effect of a β-methyl substituent on ΔE is obtained by substracting ΔE(**6Z–7**) (or ΔE(**6E–7**)) from the analogous ΔE-(**4–5**) (see $\Delta\Delta E$(β-CH$_3$) values in Table VI). The following features are obtained: (a) In both series ΔE is smaller for the aldehyde than for the ketones. (b) In the Z series a β-methyl increases ΔE by 1.2–1.5 kcal mol^{-1} for R = H, Me, Et, i-Pr and by 4.4 kcal mol^{-1} for R = t-Bu. In the E series the β-methyl effect is larger, especially for R = t-Bu where ΔE(**6Ee–7e**) is 20.1 kcal mol^{-1} compared with ΔE(**4e–5e**) of only 10.8 kcal mol^{-1}. (c)

(41) Kresge, A. J.; Tobin, J. B. *J. Am. Chem. Soc.* **1990**, *112*, 2805.
(42) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

β,β-Dimethyl substitution also increases ΔE. ΔE(**8a–9**) and ΔE(**8b–5d**) are larger by 1.2 and 0.8 kcal mol^{-1} than ΔE(**4a–5a**) and ΔE(**4b–5b**), respectively (i.e., ΔE(**8a–9a**) = 9.7 (3-21G), 15.6 (6-31G*) and ΔE(**8b–5b**) = 14.5 (3-21G), 19.8 (6-31G*), all values in kcal mol^{-1}).

The increase of ΔE, even in the sterically noncongested **6Z** series, is unexpected. Alkyl groups that stabilize C=C bonds[42] are expected to stabilize the enol and to decrease ΔE. The limited experimental gas-phase or solution data (Table VIII) also indicate that β-methyl substitution decreases ΔE. Thus, substitution of a β-hydrogen in **4a** and in **4b** by a methyl group *decreases* ΔE-(enol–keto) in the gas phase by 3.3–4.8 kcal mol^{-1}.[9] Kresge et al. found that in water ΔE(enol–keto) for **6b**, **6c**, and **6d** are *smaller* by 1.1, 1.8, and 1.5 kcal mol^{-1}, respectively, than for **4b**, **4c**, and **4d**.[4c] The effect of β,β-dimethyl substitution is similar; ΔE(**8a–9**) and ΔE(**8b–5d**) are smaller than ΔE(**4a–5a**) and ΔE-(**4b–5b**) by 3.2 and 1.3 kcal mol^{-1}, respectively.[4c]
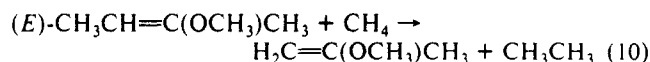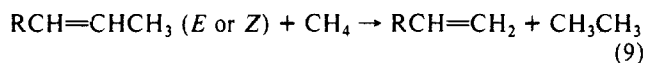
To probe the reasons for this computational–experimental discrepancy the total β-methyl effect was separated into contributions from the enols **6** (eq 6) and from the ketones **7** (eq 7); positive energies (Table IX) indicate a β-methyl stabilization. Substracting eq 7 from eq 6 gives isodesmic eq 8, which describes the total β-methyl effect on ΔE(enol–carbonyl), i.e., the $\Delta\Delta E$-(β-CH$_3$) values.

$$CH_3CH=C(OH)R + CH_4 \rightarrow$$
$$\mathbf{6Z}\text{ or }\mathbf{6E}$$
$$\quad H_2C=C(OH)R + CH_3CH_3 \quad (6)$$
$$\mathbf{4}$$

$$RC(=O)CH_2CH_3 + CH_4 \rightarrow RC(=O)CH_3 + CH_3CH_3 \quad (7)$$
$$\mathbf{7}\qquad\qquad\qquad\qquad\mathbf{5}$$

$$CH_3CH=C(OH)R + RC(=O)CH_3 \rightarrow$$
$$\mathbf{6Z}\text{ or }\mathbf{6E}\qquad\qquad\mathbf{5}$$
$$\quad H_2C=C(OH)R + RC(=O)CH_2CH_3 \quad (8)$$
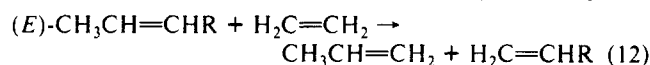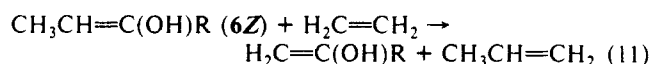$$\mathbf{4}\qquad\qquad\qquad\mathbf{7}$$

For the enols (eq 6), where experimental data are lacking, the calculations show that with all α-R substituents, except for t-Bu, a β-Me cis to OH is stabilizing by 1.7–2.2 kcal mol^{-1} (at 3-21G, or at 6-31G*). However, these stabilization energies even in the less crowded **6Z** series are *less than half* of the experimental β-Me stabilization energies of ca. 4.5–5.9 kcal mol^{-1} (and the very similar computed energies) in the analogous alkenes (eq 9).[42] Reduced β-Me stabilization in the enols is supported by thermochemical data for the closely related methyl ether of **6Eb**, for which eq 10 is endothermic by only 1.9 kcal mol^{-1}.[43]

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$$RCH{=}CHCH_3 \ (E \text{ or } Z) + CH_4 \rightarrow RCH{=}CH_2 + CH_3CH_3 \tag{9}$$

$$(E){-}CH_3CH{=}C(OCH_3)CH_3 + CH_4 \rightarrow$$
$$H_2C{=}C(OCH_3)CH_3 + CH_3CH_3 \tag{10}$$

Equation 11, which compares the β-Me effect in enols **6Z** and in propene, is uniformly exothermic, emphasizing that the β-Me/OH interaction is destabilizing. This conclusion is supported by experimental data[42] showing that eq 12, R = H, Me, Et, *i*-Pr, *t*-Bu, is nearly thermoneutral, in contrast to eq 11. The small stabilizing β-Me effect indicated by eq 6 results from comparison of the C(sp²)–Me bond in **6** with the weaker C(sp³)–Me bond in ethane.
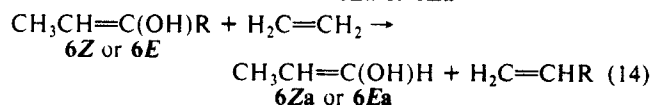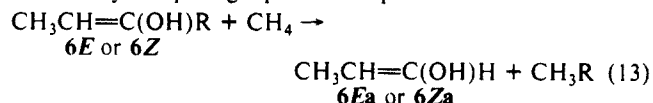
$$CH_3CH{=}C(OH)R \ (\mathbf{6Z}) + H_2C{=}CH_2 \rightarrow$$
$$H_2C{=}C(OH)R + CH_3CH{=}CH_2 \tag{11}$$

$$(E){-}CH_3CH{=}CHR + H_2C{=}CH_2 \rightarrow$$
$$CH_3CH{=}CH_2 + H_2C{=}CHR \tag{12}$$

Surprisingly, a β-methyl substituent also stabilizes the ketones by 2.3–3.4 kcal mol⁻¹ (experimental data;[42] our theoretical values (eq 7) are in excellent agreement; Table IX). Thus, *the theoretical prediction that a β-methyl group increases ΔE (eq 8) results from a larger stabilizing β-methyl effect in the ketones than in the enols.*

Careful examination of the gas-phase data, which contrary to the computations point to a substantial *decrease* in ΔE by β-Me substitution,[9] reveals possible difficulties. Using experimental ΔH_f° values[9] we calculate for eq 6 when R = H, Me stabilization energies of 7.5–8.7 kcal mol⁻¹ (Table IX). These values are much higher than the calculated values (Table IX), or the experimental effects in simple alkenes (eq 9) or in (E)-2-methoxy-2-butene (eq 10). As we see no theoretical reason why the β-Me effect in enols should be substantially higher than that in the other systems we infer that Tureček's estimates[9] of the β-Me effect in enols are by ca. 5 kcal mol⁻¹ too high. This also explains why these measurements[9] show a relatively large reduction in ΔE(6–7) compared with the corresponding ΔE(4–5). *We conclude that the calculations reproduce correctly the β-Me effect both in the C=O compounds and in the enols, and that the experimental gas-phase measurements are less reliable.*

The experimental data (Table VIII) point to a *reduction* in ΔE(enol–carbonyl) by β-Me substitution also in water, but the effect is significantly smaller (ca. 1.1 kcal mol⁻¹ for a single methyl)[4d] than that claimed in the gas phase.[9] The difference between the gas-phase calculations and the effect in water is only ca. 3 kcal mol⁻¹. The β-Me effect in water was attributed to the stabilizing effect of alkyl groups on C=C bonds,[4d] but our calculations suggest that the small decrease in ΔE in water by β-Me substitution is due to solvation.

Comparison of the effects of the α-R group in **6** (eq 13, Table IX) and in **4** (eq 3, Table VII) shows that in the **6Z** series the α-alkyl effect is almost the same with either β-Me or β-H, except for R = *t*-Bu where stabilization is reduced by 3.9 kcal mol⁻¹ due to increased *cis*-Me/OH steric interactions in **6Z**e. Steric interactions are more pronounced in the **6E** isomers and particularly in **6E**e where an α-*t*-Bu destabilizes the enol by 1.9 kcal mol⁻¹, while it stabilizes **4e** by 6.8 kcal mol⁻¹. Similar conclusions are reached by comparing eq 14 with eq 5.
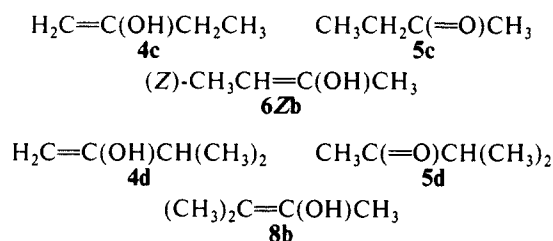
$$CH_3CH{=}C(OH)R + CH_4 \rightarrow$$
$$\mathbf{6E \text{ or } 6Z}$$
$$CH_3CH{=}C(OH)H + CH_3R \tag{13}$$
$$\mathbf{6Ea \text{ or } 6Za}$$

$$CH_3CH{=}C(OH)R + H_2C{=}CH_2 \rightarrow$$
$$\mathbf{6Z \text{ or } 6E}$$
$$CH_3CH{=}C(OH)H + H_2C{=}CHR \tag{14}$$
$$\mathbf{6Za \text{ or } 6Ea}$$

Table X. Calculated Relative Energies (kcal mol⁻¹) of Isomeric Enols[a,b]

compd	rel energy		compd	rel energy	
	3-21G	6-31G*		3-21G	6-31G*
4b	0.0	0.0	**4c**	0.0	
6Ea	4.1	4.1	**6Zd**	0.2	
4d	0.0	0.0	**4c**	0.0	0.0
6Zc	1.6		**6Zb**	0.4	−0.8
8b	3.7	0.9	**8a**	3.7	2.8

[a] Total energies can be found in the supplementary material. [b] Using the 3-21G optimized geometries.

d. Isomeric Enols. For unsymmetrically substituted ketones enolization can sometimes give more than one enol. Our data enable to probe the energy differences between isomeric enols in the cases of **5c/4c–6b** and **5d/4d–8b**. The calculations predict

$$H_2C{=}C(OH)CH_2CH_3 \qquad CH_3CH_2C({=}O)CH_3$$
$$\mathbf{4c} \qquad\qquad\qquad \mathbf{5c}$$
$$(Z){-}CH_3CH{=}C(OH)CH_3$$
$$\mathbf{6Zb}$$

$$H_2C{=}C(OH)CH(CH_3)_2 \qquad CH_3C({=}O)CH(CH_3)_2$$
$$\mathbf{4d} \qquad\qquad\qquad \mathbf{5d}$$
$$(CH_3)_2C{=}C(OH)CH_3$$
$$\mathbf{8b}$$

(Table X) that **6Zb** is more stable than the isomeric **4c** by 0.8 kcal mol⁻¹ (6-31G*//3-21G, −0.3 kcal mol⁻¹ at 3-21G//3-21G) and will therefore dominate in the equilibrium with **5c**. In contrast **4d** is calculated to be 0.9 kcal mol⁻¹ (6-31G*//3-21G) more stable than **8b** and thus will dominate in the equilibrium with **5d**. It should be noted that the 3-21G basis set overemphasizes the stability of α-substituted enols (**4**) relative to the isomeric β-substituted enols (**6** and **8**). Gas-phase experimental data for comparison are lacking, and in water, **6b** (stereochemistry undefined) and **8b** are both more stable by 1.7 kcal mol⁻¹ than **4c** and **4d**, respectively.[4b]

Calculated relative energies of non-tautomeric isomeric enols are also collected in Table X. The α-methyl-substituted enols **4b** and **6Zb** are calculated to be more stable than the isomeric β-substituted enols **6Ea** and **8a** by 4.1 and 3.6 kcal mol⁻¹, respectively. Experiments in the gas phase give the same stability order but the energy difference is only 1.7 kcal mol⁻¹.[9,44] Higher level calculations and more precise experiments are required to establish the correct values.

(43) Using the following experimental ΔH_f° (kcal mol⁻¹): (E)-CH₃CH=C(OCH₃)CH₃, −39.9;[le] CH₂=C(OCH₃)CH₃, −35.8;[le] CH₄, −17.8;[42] C₂H₆, −20.0.[42]

(44) Using ΔH_f° (**4b**) = −42.1 kcal mol⁻¹, in preference to the value of −40.6 kcal mol⁻¹.[9] According to the latter value ΔE(**4b–6Ea**) = 0.[9]