J. Org. Chem. 1986, 51, 2539–2544

Winnik.[18] 1-Hexadecene (Aldrich, 94%) and 1-tetradecene (Aldrich, 92%) were used as received for detection of cleavage products.

n-Octadecyl *trans*-cinnamate (1), mp 47–49 °C (lit.[3] mp 48–50 °C), *n*-hexadecyl *trans*-cinnamate (2), mp 39.6–40.6 °C, and *n*-tetradecyl *trans*-cinnamate, mp 29.5–31.5 °C, were synthesized and purified following reported procedures.[4,7] The cis isomers of 1–3 were formed by irradiating nitrogen saturated solutions (5×10^{-4} M) of 1–3 in *n*-hexane.[10] Aliquots were withdrawn periodically and analyzed by HPLC until a constant trans/cis ratio was obtained. The presence of the cis isomer in the irradiated samples was confirmed by ^{1}H NMR of the residues, obtained after removal of solvent.

The ^{1}H NMR ($CDCl_3$) of *trans*-1 is reported below along with that of *cis*-1. The *cis*-1 spectrum was obtained by difference, removing the peaks (at appropriate intensities) from the spectrum of the mixture. *trans*-1: ^{1}H NMR ($CDCl_3/Me_4Si$) δ 0.89 (t, 3 H, J = 6 Hz), 1.2–1.8 (m, 32 H), 4.2 (t, 2 H, J = 6.7 Hz), 6.43 (d, 1 H, J = 16.0 Hz), 7.35 (m, 5 H), 7.68 (d, 1 H, J = 16.0 Hz). *cis*-1: ^{1}H NMR ($CDCl_3/Me_4Si$), δ 0.89 (t, 3 H) 1.2–1.8 (m, 32 H), 4.09 (t, 2 H, J = 6.7 Hz), 5.94 (d, 1 H, J = 12.7 Hz), 6.96 (d, 1 H, J = 12.7 Hz), 7.5 (m, 5 H).

Characterization of the α-Truxillate (5) and δ-Truxinate (6) Dimers of 1–3. The procedure for the dimers of 1 is described. The α-truxillate and δ-truxinate dimers were synthesized by solid-state photodimerization of the α and δ crystal forms of 1 as reported.[4] The α-truxillate and δ-truxinate dimers obtained from the irradiation of 1 in BS had the same retention volumes as those of the correspondingly synthesized dimers.

Further confirmation of the α-truxillate and δ-truxinate dimers of 1 was obtained by hydrolyzing the dimer diesters[6] and detecting the diacids by HPLC. Samples irradiated in BS were first subjected to preparative TLC (silica gel, 50:50 chloroform–*n*-hexane) to remove BS. The resulting material, a mixture of the starting cinnamate and the dimers, was dissolved in hot 95% ethanol and added to an equimolar amount of sodium hydroxide dissolved in 95% ethanol. The solution was stirred at 70 °C for 15 min, and then the excess ethanol was removed by distillation. Water was added to the resulting solid to dissolve the sodium salts of cinnamic acid, α-truxillic acid, and δ-truxinic acid. The long-chain alcohol precipitated from the aqueous solution upon cooling and was filtered. The filtrate was carefully acidified (10% aqueous HCl) to precipitate the mixture of organic acids. The solid was filtered, dissolved in methanol, and identified by comparison of HPLC retention volumes during separate injections and coinjections with authentic dimers. The α-truxillate and δ-truxinate natures of the dimers from 2 and 3 were confirmed similarly.

Detection of Cleavage Products. Products arising from ester cleavage of 1–3 (*trans*-cinnamic acid, 1-octadecene, 1-hexadecene, and 1-tetradecene) were detected on C_{18} and silica HPLC columns, and their identities were confirmed by coinjection with known samples.

Irradiations. Solutions of 1, 2, and 3 in BS were prepared by vigorously stirring the components at ca. 30 °C. The viscous liquids were viewed under a microscope with polarizing lenses to ascertain homogeneity: samples with microcrystallites display a distinct pattern. Phase-transition temperatures were measured for each concentration of cinnamate in BS. Solutions of cinnamates in BS were placed in 0.04-cm path length Kimax cells which were flame-sealed under vacuum (3×10^{-4} torr). Samples were thermostated for at least 10 min prior to being irradiated with a Hanovia 450-W medium-pressure mercury lamp fitted with a Pyrex filter. After irradiation, the contents of the cells were dissolved in chloroform and products were analyzed by HPLC. No correction was made for the difference in detector response between dimers and monomers at 254 nm.

Determination of Relative Quantum Efficiency for Photoreaction of 1 and 2 in the Liquid–Crystalline and Isotropic Phases. Four 30-mg samples of 1 and 2 in BS (40% by wt) were prepared as described earlier and sealed in Kimax cells whose exposed surface area was matched. One pair of samples (one each of 1 and 2) was irradiated together at 18 °C for 15 min, and the other pair was irradiated at 32 °C (as soon as the bath temperature had been raised and equilibrated) for 4 min, under otherwise identical conditions. The samples were then analyzed as before by HPLC and the percent conversion per unit of irradiation time taken as the relative quantum efficiency normalized to the isotropic value of 1 (see Table I).

Acknowledgment. We thank the National Science Foundation for its support of this work (Grant CHE 83-01776).

Registry No. 1, 61415-12-1; 2, 102260-50-4; 3, 102260-51-5.

Spectra of Isomeric Enols

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Received December 31, 1984

The NMR and IR spectra of two isomeric nonequilibrating enols are investigated with regard to current theories of strongly hydrogen-bonded systems and to theories concerning possible ring current in hydrogen-bonded enol systems. No evidence is found for ring current. The results of the spectral studies are compared to MM2 calculations of structure. The latter predict little stabilization for the enolic hydrogen bond, in contrast to experimental results. The results of recent modifications of MM2 enabling a better approximation of the hydrogen bonds are reviewed.

Keto–enol tautomerism is an integral part of many reactions involving carbonyl compounds, although the enol forms, per se, rarely have been studied.[1] In the last century, Claisen, Wislicenus, Knorr, Hantzsch, and Knoevenagel and their co-workers were able to isolate enols by crystallization.[2-7] The classic work of Meyer and co-

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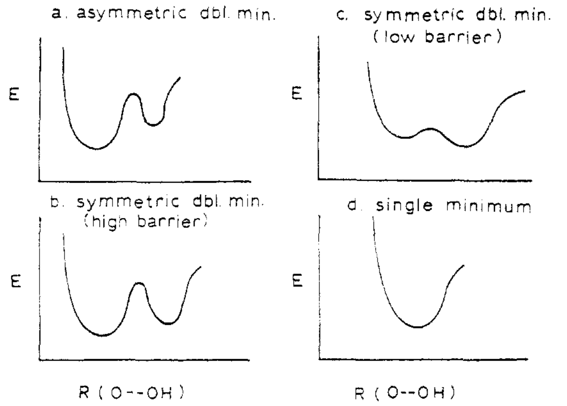


Figure 1. Potential functions of the various hydrogen-bond types.

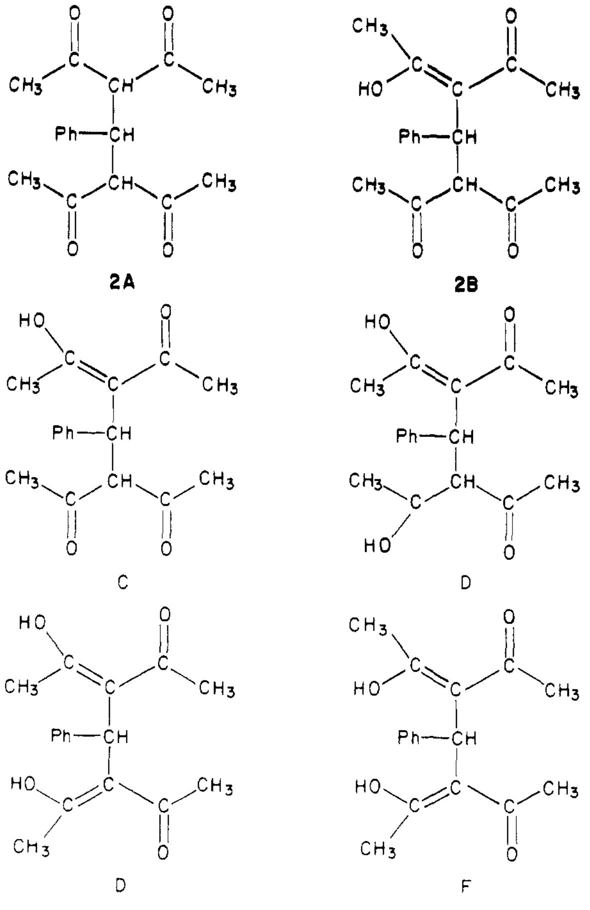
workers involved estimation of the enol content of various ketones through physical separation by distillation in quartz apparati.[8,9]

More recently, nonintrusive spectroscopic techniques have been applied to studies of enols.[10-12] Oxygen-17 NMR has been a particularly useful tool in studies of hydrogen bonds, showing that both oxygens of the hydrogen-bonded (H-bonded) structure are electron rich, in agreement with theory.[12]

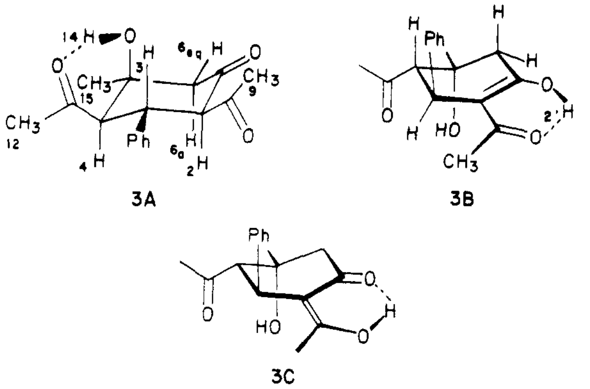
Theoretical studies of H-bonded enol systems have focused on the shape of the potential well.[1,13,14] As a result of extensive studies on enols, Shapet'ko et al. have suggested that "single minimum" H-bond types are of importance (cf. model d, Figure 1). The hydrogen is equally shared by both oxygens.[14] In other studies, it was estimated that the barrier for hydrogen transfer between oxygens is at least 6 kcal/mol, giving a double minimum well, as in model c.[15] In either case, the early studies are called into question, as physical isolation requires a very high barrier (cf. models a or b).

In the H-bonded enol form of β-diketones, the extreme deshielded hydroxyl signal (ca. δ 16)[16] has been ascribed to ring current, involving a vacant high-energy p orbital on hydrogen.[17-19] In the present study, we hoped to find additional data relating to this interesting postulate.

Scheme I



Scheme II



Another question concerns the ability of force-field calculations to define H-bonded structures accurately. The

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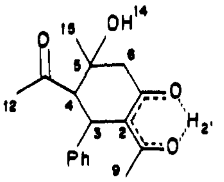
Table I. ^1H NMR Chemical Shifts and Coupling Constants



H	chemical shifts, ppm 3A	3B (endo)	3C (exo)
H2 or H2′	3.80	16.2	16.2
H3	3.98	4.10	4.06
H4	3.27	2.87	3.11
OH(14)	3.98	3.57	2.18
H6	2.63	2.52	2.51
H6′	2.53[a]	2.56[b]	2.86[b]
$COCH_3$(9)	2.02	1.62	1.87
$COCH_3$(12)	1.66	1.67	1.67
CH_3(15)	1.31	1.25	1.37
	Coupling Constants, Hz		
$^3J_{1,2}$	12.3		
$^3J_{3,4}$	11.8	10.7	10.7
$^4J_{6_a,14}$	2.6		
$^2J_{6_a,6_e}$	−14.3	−16.8[c]	−17.4

[a] Axial hydrogen, split by OH. [b] Slightly coupled to OH (line broadened only). [c] Value approximate due to closely spaced resonances.

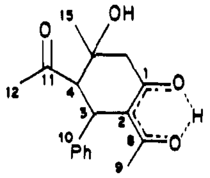
widely used MM2 program, as well as other types of force-field calculations, considers an H-bond to be an electrostatic interaction.[20-22] This interpretation is supported by a number of theoretical treatments.[23,24]

Knoevenagel and co-workers claimed to have isolated six compounds from the condensation of benzaldehyde with 2,4-pentanedione (Scheme I).[7] Later Rabe and Elze and also Knoevenagel realized that such 1,5-diketones often are cyclized due to an internal aldol condensation.[7c] However, the cyclic structure is unlikely for double enols, as one enol would not be conjugated. The object of the present study is to isolate as many of these compounds as possible and to study the characteristics of the H-bonded system by spectroscopic means in conjunction with force-field calculations. It is of particular interest to compare the enolic H-bond with an ordinary H-bond in these molecules.

Although Knoevenagel's procedures were not particularly detailed, these procedures were essentially correct regarding isolation of three compounds. Modern chromatographic techniques were unsuccessful in our hands (isomerization appeared to occur). Compound **3A**, which was isolated in the highest yield, proved to have cyclic triketone structure (cf. Scheme II). The infrared spectrum showed a broad peak at 3440 cm^{-1}, indicative of a moderately strong H-bond between the hydroxyl at C5 and the neighboring carbonyl group.[25] The NMR data are recorded in Tables I and II for isomer **3A** and related compounds.

The ^1H NMR coupling constants $^3J_{1,2}$ and $^3J_{2,3}$ of 12–13 Hz indicate trans vicinal hydrogens. The major substituents at C2, C3, and C4 are thus equatorial. The long-range coupling of hydroxyl to H_{6_a} (2.6 Hz) through the *W* configuration is indicative of restriction of exchange due to H-bonding.[26]

Table II. ^{13}C NMR Absorptions



C	chemical shift, ppm 3A	3B (endo)	3C (exo)
1	204.9	178.5	198.9
2	67.3	109.2	108.4
3	44.9	44.2[a]	43.1
4	61.3	63.4	65.0
5	74.1	68.6	70.6
6	53.1	44.0[a]	47.9
CH_3(9)	29.7	26.8	22.2
CH_3(12)	33.6	34.2	34.6
CH_3(15)	27.7	27.8	26.4
CO(8)	204.9	198.3	178.9
CO(11)	216.2	213.7	208.3

[a] Tentative assignments.

The methyl resonances were assigned from NOE data.[27] On irradiation of CH_3(12), an 8% increase in integration (14% increase in peak intensity) of H4 is observed, thus indicating close proximity of these groups, imposed by the H-bond. Similarly, irradiation of CH_3(9) affected only H2 (20% increase in intensity). Irradiation of CH_3(15) failed to affect H3a, indicating that this methyl is equatorial.

The magnitude of the geminal proton coupling ($^2J_{6_a,6_e}$ = −14 Hz) is consistent with a relatively pure chair form for the six-membered ring.[28] The angular relationship of the methylene hydrogens with carbonyl is such that a relatively small contribution to ^2J occurs through interaction with carbonyl (vide infra).

Isomer **3B** proved to be one of the enols, as indicated by the extreme deshielding of the enolic hydroxyl (δ 16.2).[19b] The very sharp absorption is in marked contrast to the broad peaks found with exchanging enolic hydrogens reported in the literature.[16] In **3B**, no coupling is observed to either hydroxyl. The enolic hydroxyl showed the expected broad IR absorption at 2400–2800 cm^{-1}, whereas the other hydroxyl is found at 3520 cm^{-1}, i.e., more weakly H-bonded than in **3A**. The carbonyl absorptions in **3B** (1705 and 1640–1600 cm^{-1}) also show the effects of H-bonding and conjugation in comparison to similar groups in **3A** (1725 and 1705 cm^{-1}). The deformation of the ring in the enol weakens the H-bond for OH(14), thus facilitating exchange of the hydroxyl protons.

The decision as to whether **3B** is an endocyclic or exocyclic enol rests upon mass spectrometric evidence, in conjunction with ^{13}C NMR.[29] The third compound isolated (**3C**) also proved to be an enol, and a comparison of the two structures, at this point, is of interest. The ^{13}C shift of the conjugated carbonyl is not informative (179 ppm in both **3B** and **3C**). However, the groups neighboring carbonyl displayed quite different shifts. In a model compound, 2,4-pentanedione, the methyl at 30 ppm shifts

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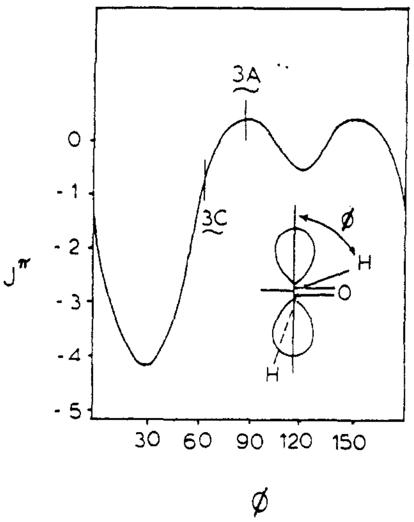

Figure 2. Dependence of $^2J_{gem}$ on angle with respect to carbonyl p orbitals.

to 24 ppm in the equilibrating enol.[30] Since a given methyl neighbors C=C(OH) only half the time, the shift is probably larger in a nonequilibrating structure. In moving from **3A** to **3B**, C6 is strongly shifted (53 → 44 ppm). The corresponding shift in moving from **3A** to **3C** is much less (53 → 47 ppm). In contrast, the acetyl methyl group (CH_3(9)) is more strongly shifted in **3C** (30 → 22 ppm) compared to **3B** (30 → 27 ppm). The ^{13}C spectra strongly suggest that **3B** possesses an endocyclic C=C and **3C** an exocyclic C=C(OH)CH_3 group.

In ^1H NMR studies of similar compounds, an upfield shift for methyl groups adjacent to the enolic C=C was found by the Forsen.[1] The data in Table II are difficult to interpret in terms of this model, as the shifts involved are small and not uniform. The marked change in conformation of the six-membered ring on enolization also is a factor in the change in chemical shifts. In the mass spectrum (cf. Experimental Section), it is quite clear that acetyl loss (presumably the C2 acetyl) is prevalent for **3A** and **3B** but much less for **3C** in which the acetyl has become a C=C(OH)CH_3. Full mass spectrometric data will be reported separately.[29] The mass spectroscopic data are in agreement with the ^{13}C NMR data in supporting an endocyclic double bond for **3B** and an exocyclic double bond for **3C**.

Since formation of the H-bonded structures in either **3B** or **3C** appears to involve the C2 CH_3CO or C=C(OH)CH_3 group jammed into the C3 phenyl group, a strong steric shift for methyl is expected in the ^{13}C spectra. As Table II shows, the shift is small, i.e., ca. 3 ppm for **3B**. MM2 calculations showed that a drastic change in conformation occurred on forming either enol. In these boat forms, little interference between methyl and phenyl exists (cf. Figure 3). The other aspect of the ^{13}C spectra of interest is the steady drop in chemical shift of the H-bonded acetyl carbonyl, CO(11), (**3A**, 216 ppm; **3B**, 214 ppm; **3C**, 208 ppm). These changes are consistent with the weakening of the H-bond to hydroxyl due to ring deformation.[26] In both **3B** and **3C**, the vicinal coupling constant, $^3J_{3,4}$ = 10.7 Hz, is significantly lower than that of **3A** (11.8 Hz), indicative of ring flattening. In isomer **3C**, the very large $^2J_{6_a,6_e}$ = −17.4 Hz is consistent with a flattening of the ring compared to **3A**. The geometry of the C6 methylene hydrogens with respect to CO(1) more nearly approximates their "bisected geometry" (cf. ref 28). The pseudo p orbitals of CH_2 overlap efficiently with the carbonyl p orbitals, thus imparting negative increment to ^2J (Figure 2). In **3B**, $^2J_{6_a,6_e}$ = −16.8 Hz is found.

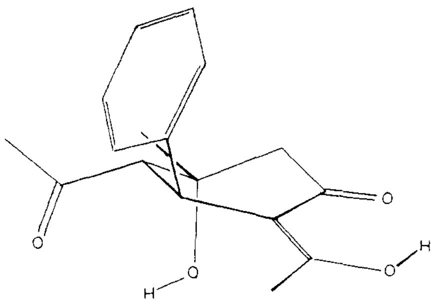

Figure 3. Geometry of the enol **3C**, as determined by MM2 calculations.

In isomer **3B**, a NOE was possible only for CH_3(15) because of the closeness to one another of other absorptions. Irradiation of CH_3(15) caused an increase in intensity of the neighboring CH_2 group (5%), of OH, and of H4 but not for the transannular H_{5_a}. Thus, CH_3(15) is equatorial. However, 2D NOE experiments showed more extensive but weak magnetization transfer.

In **3C**, the hydroxyl, OH(14), is shifted upfield compared to the other two isomers (to 2.2 ppm), consistent with the ^{13}C data. Irradiation of CH_3(8) produced enhancements for H4 and H5. Irradiation of CH_3(15) affected only H4 and H6.

With respect to the question of ring current of the H-bonded enol system, the extreme deshielding of the enolic hydroxyl is evident in both isomers. However, the change in chemical shift of adjacent hydrogens, H3 and H6, in either enol is weak. Thus, no consistent evidence for ring current seems evident. In view of the location of the enolic hydrogen off-center of the O–O internuclear line (cf. Figure 3), it is questionable whether the hydrogen p orbital could be involved. The anisotropy changes due to the O–O interaction may be responsible for the extreme deshielding of the hydrogen.[19b]

Molecular Mechanics Calculations. Initially, MM2 calculations were performed on the C3 methyl analogues (**5A–C**) of the phenyl-substituted compounds **3A–C** of the present study, as methyl has about the same radius as phenyl (π system). This was done in order to save calculation time, as phenyl-substituted compounds are troublesome. However, the geometries of **5B**,**C** were not in agreement with NMR data. Thus, the original compounds **3A–C** were calculated, without undue difficulty due to phenyl in this particular case. The change in substituent markedly affected geometry and energy. For the methyl-substituted compounds, the exocyclic and endocyclic enols have about the same steric energy. For the phenyl-substituted compounds, the endocyclic isomer is predicted to be more stable than the exocyclic isomer **3C**, in agreement with the work of Garbisch.[31] The dihedral angle H4–C–C–H5, 150–160°, is in reasonable agreement with the 10-Hz NMR coupling constants in **3B** and **3C** (**5B** and **5C** are predicted to have a 120–130° dihedral angle).

Molecular models of the enol **3C** indicate that the C2 acetyl methyl group interferes with the C3-phenyl group. MM2 predicts that the molecule occupies a near-boat form (cf. Figure 3), in which the phenyl–acetyl interaction is avoided. However, other destabilizing interactions are

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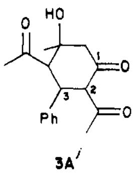
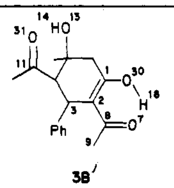
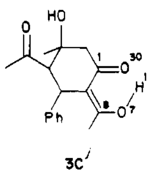
Table III. Molecular Mechanics Calculations

	 3A[j]			 3B[j]			 3C[j]		
	N[b]	DK2[c]	DK4[c]	N	DK2	DK4	N	DK2	DK4
steric energy[a]	13.0	12.2	10.5	12.9	13.1	13.7	15.3	15.3	15.9
bond compression	1.5	1.4	1.3	1.8	1.6	1.5	1.9	1.7	1.5
angle bending	1.9	1.7	1.4	4.5	4.6	4.2	4.9	5.1	4.5
van der Waals'									
1,4-interactions	14.2[d]	13.6	13.7	15.7[e]	14.7	14.8	15.8[f]	14.7	14.8
other interactions	−5.9	−5.2	−5.7	−2.7	−2.5	−3.5	−2.4	−2.3	−3.4
torsional interactions	−1.0[g]	−2.1	−1.8	−2.6[h]	−2.6	−2.2	−1.2[i]	−1.1	−0.5
dipolar interactions	2.0	1.9	1.3	−4.0	−3.0	−1.2	−4.1	−3.0	−1.1

[a] Steric energy is the overall energy excluding resonance contributions (in kcal/mol). [b] Normal MM2 parameterization (dielectric constant presumably is 1.0). [c] Dielectric constant is 2 or 4 as indicated; the lone pair radius has been reduced to 0.6 Å, with ϵ equal to 0.008. Results with the lone pair radius at 0.8 Å are about the same in steric energy. [d] Broken down further as follows: C1–O13, 0.3; C8–O30, 0.55; O30–C6H_2, 0.42; Ph–C11, 0.45; H14–O31, 0.49. [e] Breakdown: OH18–O7, 1.2; O30–O7, 0.97; C8–O30, 0.4; C1–O7, 0.9. [f] Breakdown: OH18–O30, 1.2; O7–O30, 0.97; C8–O30, 0.8; C1–O7, 0.7. [g] Torsional angles: 2–3–4–5, 54.9°; 3–4–5–6, −57.5°. [h] Torsional angles: 2–3–4–5, −33°; 3–4–5–6, +60°. At DK4, 2–3–4–5, −39°; 3–4–5–6, 62°. [i] Torsional angles: 2–3–4–5, −22°; 3–4–5–6, 55°. [j] **5A–C** were calculated to have steric energies of 14.8, 16.5, and 16.5 kcal/mol, respectively.

introduced in going to a boat form (cf Table III). The energy of the keto form **3A** is surprisingly close to that of the enol **3B**, despite the fact that the keto form occupies a classic chair form and the enol a virtual boat form. The "dipolar interactions" term of MM2 is almost 6 kcal more favorable for the enol than for the keto form. However, these dipolar interactions would be attenuated in polar solvents leading to a preference for the keto form. In the gas-phase ion chemistry, most results are consistent with a dominance of enol forms.[32]

The calculations do not present as believable results with regard to H-bonding. The enolic H-bond is more favorable than the geometry with the OH rotated 180° because the latter is destabilized through lone pair interactions with carbonyl. The enolic H-bond is calculated to have little overall stability, and in fact, some difficulty was encountered in making the program accept the H-bonded geometry. The enolic H-bond is calculated to be slightly less stable than the C4-acetyl–C5-hydroxyl H-bond contrary to a great deal of precedent. The IR data suggest a much stronger H-bond for the enol. However, these MM2 calculations do not take into account the effect of conjugation in the extended enol π system. A MMP1 calculation suggests ca. 5 kcal as the additional stabilization due to conjugation.

In **3B,C** the interaction between the enolic hydroxyl and carbonyl is attractive (−1.7 kcal). The same stabilization is found for the other H-bond. This favorable energy is diminished by steric and bending terms; e.g., the interaction of the ketone oxygen with the enolic OH is destabilizing by 1.2 kcal, according to the parameterization of the program. Similarly, in both enols, the congested nature of the enol leads to a repulsion between C1 and O7 of ca. 0.8 kcal and also between C8 and O30 of ca. 0.6 kcal. In addition, the oxygens themselves are repulsive by 1 kcal. The deviation of the bond angles of the ketone carbonyl also reflect the congestion in the enolic region. Thus, the C6–C1–O30 angle from ca. 120° to 112° reflects an effort of the two oxygens to avoid one another. The net effect would be little stabilization due to the enolic H-bond, per se.

Kroon-Batenburg and Kanters,[33] following Taylor,[34] and also Kollman and co-workers,[35] have suggested alternative ways of treating H-bonding in force-field calculations. Kollman suggests that the drop-off of electrostatic interactions should be proportional to the distance separating the interacting groups.[35,36] This is a useful suggestion, as the present parameterization involves rather sizable electrostatic interactions of distant groups. Kroon-Batenburg and Kanters recommend a reduction of the size of the lone pairs involved in H-bond acceptance. This is difficult in the present situation as carbonyl oxygens are regarded as a united atom, without discrete lone pairs. However, this adjustment was made for the hydroxyl. This change resulted in about a 1-kcal stabilization of the enol forms and 0.6 kcal for the keto form, **3A**. In addition, Kroon-Batenburg and Kanters add new terms to the force-field equation representing the special interaction of H-bonded atoms. The net effect is a stabilization of H-bonded atoms without inordinate steric repulsions due to lone pairs interactions with approaching atoms. In our hands, these new terms led to a further divergence in energy of the two H-bonds in the enols, as the ordinary H-bond is stabilized by ca. 1 kcal whereas the enolic H-bond remains the same energy (the oxygens are too close, 2.5 Å, to permit any added stabilization, according to the parameterization of the program).

In conclusion, it appears that further work on H-bonding vis-à-vis molecular mechanics is in order. The lack of facile equilibration in the enols is probably due to the strongly off-center hydroxyl.[37,38]

Experimental Section

Preparation of 3-Hydroxy-3-methyl-5-phenyl-4,6-diethanoylcyclohexanone (3A). In this preparation and subsequent isolation of the enols, the procedures of Knoevenagel were

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follows as closely as possible.[7] Condensation of 2,4-pentanedione (10 g, 0.01 mol) with benzaldehyde (5.3 g, 0.005 mol) in 70% ethanol, catalyzed by 1 mL of piperidine gave **3A** as a precipitate after a 3-day reaction period (8.1 g, 43% yield, mp 165–169 °C). Subsequent crops could be attained on concentration of the mother liquor. The crude product was recrystallized from hot benzene, giving white crystals, mp 173–174 °C. This melting point deteriorated on standing for several days, finally giving mp 165–168 °C, similar to the behavior reported by Knoevenagel.[7]

Extraction of the Enol 3B. A portion of the crude product (6.0 g) was dissolved in 30 mL of boiling benzene to give a yellow liquid. The hot benzene solution was then poured into a beaker and left to cool for about 12 h. White crystals precipitated on cooling. After 12 h the white crystals were filtered and washed with a small amount of benzene, giving **3A**, mp 173–174 °C. The filtrate from this benzene extraction was then evaporated on a steam bath until about three-fourths the original volume remained. The solution was set aside to cool for several days. After 3 days, fine white crystals appeared, although a rust-colored oil contaminated the crystals. The mixture was stirred for several hours to disperse the oil. The crude material was filtered and washed with a very small amount of 50% ethanol. The orangish filtrate from this was set aside. It was then evaporated until a dark brown oil remained. A small amount of water was added and the mixture warmed and stirred. This mixture was then left to cool with constant stirring; after several hours, crystals appeared. The NMR spectrum indicated that this second batch of crystals was the enol isomer **3B**, in particular, the characteristic peak at δ 16 (see Table II for other absorptions): IR 3520, 1705, 1630–1600 (chelated enolic C=C and C=O), and 1360 cm^{-1}. Freshly precipitated material (by adding hexane to a CCl$_4$ solution) had a mp of 112–114 °C, but aged crystals, even stored in the cold under nitrogen, displayed a mp of 162–164 °C. The yield in successful runs was approximately 1% in our hands, but most frequently, no enol at all was obtained. The yield could be improved by recycling aged **3A**.

Isolation of Enol Isomer 3C. The original filtrate from the mother liquor was set aside for about 1 month; after that time, the viscous rusty orange liquid was vigorously stirred and hexane added, whereupon crystals precipitated from the solution. These were filtered and washed with cold hexane, mp 122–123 °C (lit.[7] mp 125–126 °C). The NMR spectrum showed the characteristic enolic hydrogen but otherwise quite different peaks than **3B**: IR 3610, 3500, 1720, 1630–1590 (chelated enolic C=C and C=O), and 1360 cm^{-1}. The yield of this second enol was of the order of 3.5% in most successful runs, and this material appeared to be stable to storage conditions in the cold.

Spectral Determinations. The carbon-13 NMR spectra were taken on Varian XL-100 and on Bruker WB 360 instruments. The NMR of **3A** was taken in CDCl$_3$ while those of the enols **3B** and **3C** were taken in CCl$_4$ that had been treated with alumina or molecular sieves (3A). The proton NMR spectra were taken on Bruker WB 360 and Varian EM 390 instruments. The IR spectra were taken on a Perkin-Elmer PE 283 instrument; spectra were run in CCl$_4$ solution. The spectra were also taken as thin films on NaCl plates. The major difference observed was the lack of free OH peaks. For the NOE experiments, a typical sample was run as follows: the sample was dissolved in dry CDCl$_3$ (from a newly opened bottle with the solvent passed over Al$_2$O$_3$). Dry nitrogen was passed through the solution until at least half of the original volume had evaporated. Me$_4$Si was added and nitrogen passed over just before sealing with the NMR tube cap. NOE experiments were done on the Varian EM 390. Later two-dimensional NOE runs were done on a Varian XL-200, although it was not evident how to quantify these data. Homonuclear correlation 2D experiments and *J*-coupled 2D experiments were also run on the Varian XL-200.

Registry No. **3A**, 21225-62-7; **3B**, 102340-19-2; **3C**, 102260-52-6.

The Electrochemical Reduction of Fluorenone Tosylhydrazone: Evidence Consistent with the Formation of the Tosyl Nitrene Anion Radical

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Received October 17, 1985

Fluorenone tosylhydrazone (Fl=NNHTs) undergoes one-electron reductive dehydrogenation in DMF–0.1 F (n-Bu)$_4$NClO$_4$ to give hydrogen and its conjugate base Fl=NN$^-$Ts as products. Fl=NN$^-$Ts is subsequently reduced at more negative potential to a dianion radical (Fl=NNTs$^{\bullet 2-}$) that is stable on the cyclic voltammetric time scale. On the coulometric time scale or in the presence of added proton donors (pK_a < ~29), Fl=NNTs$^{\bullet 2-}$ decomposes to give FlHNH$_2$ and TsNH$_2$ as the principal products. A pathway is proposed for the reaction of Fl=NNTs$^{\bullet 2-}$ which involves rate-determining proton abstraction by the nitrogen atom α to the fluorene moiety. Cyclic voltammetric and chronoamperometric data are presented which are consistent with the formation of the tosyl nitrene anion radical as a short-lived, unobserved intermediate.

There is currently considerable interest in the preparation and study of hypovalent ions in the gas phase.[1,2] Hypovalent ions are defined as molecular fragments that possess less than the normal number of substituents found attached to the central atom of a typical anion or cation. For example, in the nitrogen-centered series, the nitranion (R$_2$N$^-$) is the normal anion whereas the hypovalent ions include the nitrene anion radical (RN$^{\bullet -}$), the nitrene cation radical (RN$^{\bullet +}$), and the nitrene dianion (RN^{2-}).

The goal of this work was the preparation of a hypovalent anion in the tosyl nitrene series in the condensed phase. Although there are several potential routes for the preparation of these species, the one which was chosen for study here involves the electrolytic reduction of fluorenone tosylhydrazone anion (Fl=NN$^-$Ts, where Fl = 9-fluorenylidene and Ts = p-H$_3$CC$_6$H$_4$SO$_2$) to its dianion radical. Specifically, it was hoped that the dianion radical might undergo decomposition by a pathway involving nitrogen–nitrogen bond cleavage to form either the nitrene anion radical, TsN$^{\bullet -}$, or the nitrene dianion, TsN^{2-}, as an intermediate. On the basis of product studies and the results of experiments with proton donors of varying pK_a, we conclude that the electrolytic reduction of Fl=NN$^-$Ts

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