in the reactive keto form. (But in light of the proposed reactivity of tetrahedral carbinol–amine adducts in the amine-catalyzed decarboxylation[26] and enolization[27] of oxaloacetic acid, it is possible that the hydrate form can also participate in these reactions.) Leussing[28] has suggested that the formation of a dinuclear complex with hydrated α,α-dimethyl oxaloacetate can account for the inhibition of decarboxylation of this ion that is observed at high metal ion concentrations.

Acknowledgment. We are pleased to acknowledge several helpful discussions with Dr. M. Cocivera, and the support of this research by the National Research Council of Canada.

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Sterically Stabilized Enols. A Study Employing the Internal Rotational Barriers of the Destabilized Ketones[1]

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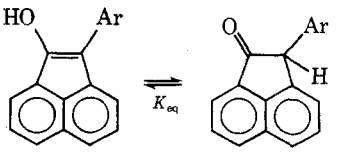
Equilibrium constants for enols 2-(2,4,6-triisopropylphenyl)acenaphthylenol (**1**) and 2-mesitylacenaphthylenol (**2**) formed from the respective sterically destabilized ketones 2-(2,4,6-triisopropylphenyl)acenaphthenone (**3**) and 2-mesitylacenaphthenone (**4**) were measured in several solvents, with maximum values of K_{eq} = 2.6 and 0.3 being observed for **1** and **2**, respectively, in Me_2SO solution. The variation of the internal rotational barrier heights as a function of the rotor's geminal substituent allows an estimate of relative ketone ground-state strain, the relaxation of which contributes the primary source of enol stability. For ketone **4** in trichlorobenzene solution, the acidity independence of the aryl site-exchange barrier and the free-energy difference between tautomers allow a determination of the lower limit of the enol's ketonization barrier as $\Delta G^{\ddagger} > 19$ kcal/mol. Enol **1**, tautomeric to the even more rotationally restricted ketone **3**, was isolated and characterized. Although the enols are of low relative free energy, a deuterium labeling experiment indicates that they are not intermediates in the pinacol rearrangement by which the respective ketones are prepared. The enols and their enolates appear useful as spectrophotometric probes of solute-solvent interactions.

Steric hindrance can selectively raise the potential energy of a keto tautomer relative to its enol form. For example, diarylacetaldehydes[3] have been sufficiently destabilized that the enols are the more thermodynamically stable tautomers. Besides increasing the energy of the keto form, steric hindrance increases the kinetic barrier to tautomerism as well; and several examples of isolable simple[4] enols of sterically hindered ketones are only kinetically stable.[5] In this category are several polyaryl enols[6] and the steroid 3β,12-dihydroxy-Δ^{12}-ursene.[7] In the present study, an examination is made of the energetics of tautomerism of sterically stabilized enols 2-tipyl-1-acenaphthylenol (**1**) (tipyl = Tip = 2,4,6-triisopropylphenyl) and 2-mesityl-1-acenaphthylenol (**2**) by studying



1, Ar = Tip
2, Ar = Mes
3, Ar = Tip
4, Ar = Mes

the barriers to internal rotation in the destabilized ketones 2-tipylacenaphthenone (**3**) and 2-mesitylacenaphthenone (**4**), respectively. As was indicated by this study, enol **1** is isolable.

Results and Discussion

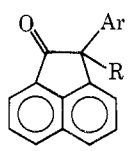
The enol and destabilized keto forms are of comparable energy, the predominance of either being controlled by choice of solvent. In solvents which cannot accept hydrogen bonds, the ketones predominate, the enols existing in only trace concentrations. However, in hydrogen-bond accepting solvents, the colorless ketones give solutions which are orange, the color of the enols.[8] The equilibrium constants, K_{eq}, for the formation of the enols decrease qualitatively as a function of solvent in the order Me_2SO > DMF > EtOH > HOAc > hexane, which is the expected order of H-bond accepting ability.[9] For enol **1**, the visible absorption maximum at 440 nm allowed the K_{eq} to be estimated as 2.6 (in Me_2SO), 1.0 (DMF), 0.25 (EtOH), 0.17 (HOAc/HCO_2H), and ≤0.004 (in hexane). For enol **2**, an equilibrium constant of K_{eq} = 0.3 in Me_2SO-d_6 solution was determined by the NMR spectrum.

Table I. Rotational Barriers and Relative Ground-State Strain [a]

Compd, R group	Barrier height, $\Delta G^{\ddagger}$, kcal/mol	Coalescence temp, °C	Ground-state strain,[b] ΔG, kcal/mol
3, R = H	≥24	≥200	
5, R = OH	14[c,d]	1	≥10
7, R = Ph	12[c,e]	−44	≥12
4, R = H	23	183	
6, R = OH	13[e]	−9	10

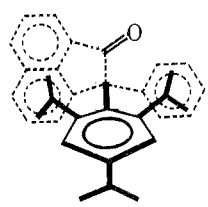
[a] Solvent was TCB and exchanging nuclei were methyl protons unless otherwise noted. [b] Relative to the ketone with R = H. [c] Exchanging nuclei were the meta ring protons. [d] Acetone-d_6 solvent. [e] $CDCl_3$ solvent.

The height of the internal rotational barrier as a function of ketone structure serves as a measure of ketone destabilization energy. The use of a rate process in this manner allows the observation of a broad range of destabilization free energy due to the exponential dependence of rate on temperature, which is broadly variable. The barrier heights displayed in Table I for ketones **3–7**,[11] in which the size of the rotor's geminal substituent R is varied, were derived from the first-order rate constants for nuclear site exchange[12] and the Eyring



5, Ar = Tip; R = OH
6, Ar = Mes; R = OH
7, Ar = Tip; R = Ph

equation.[13] The standard probe temperature NMR spectra[14] of the series establish unambiguously a common rotational ground state having the plane of the aryl ring approximately perpendicular to the acenaphthenone C_1–C_2 bond. Thus the decreasing barrier heights in the order **3** > **5** > **7** and **4** > **6** reflect an increasing ground-state strain in the same order.[16] The great sensitivity of the system to the size of the R substituent, as demonstrated by the 10 kcal/mol increase in free energy when R is changed from H to OH, suggests that the system is highly strained even when R = H. (If the rotor and H were well separated in the ground state, one might expect zero strain increase if H were changed to OH.) The >12 kcal/mol (relative to R = H) interaction when R = phenyl is of special interest: the relationship of the outside ortho alkyl group to phenyl is analogous to the relationship of the inside ortho group to the naphthalene nucleus, and it is the relaxation of this interaction which is apparently the primary source of enol stability.



7

The rate of internal rotation in ketones **3** and **4** sets an upper limit for the rate of enolization. Site exchange (designated here as ketone → ketone*) can occur via two competing processes: (1) a simple 180° rotation, and (2) enolization followed by ketonization of the symmetric enols.

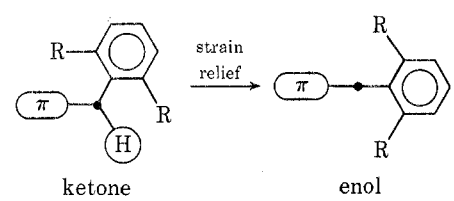
$$\text{ketone} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{ketone}^* \qquad (1)$$

$$\text{ketone} \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} \text{enol} \underset{k_1'}{\overset{k_{-1}'}{\rightleftharpoons}} \text{ketone}^* \qquad (2)$$

The observed rate constant for exchange is $k_{obsd} = k_1 + k_1'/2$, the rate of enolization necessarily being twice the rate of exchange via process 2 since the enol intermediate is partitioned equally between reversion to unexchanged ketone and inversion to site-exchanged ketone. However, identical coalescence temperatures were observed for ketone **4** in 1,2,4-trichlorobenzene (TCB) solution whether the experiment employed neutral solvent or solvent containing as much as 2% trichloroacetic acid. If the $k_1'/2$ term of the k_{obsd} equation had amounted to as much as 25 s^{-1}, a decrease in the coalescence temperature of 3 °C would have been required and would have been observed with certainty by this method. Hence the enolization pseudo-first-order rate constant k_1' must have an upper limit of 50 s^{-1}, which at 183 °C corresponds to an activation energy of $\Delta G^{\ddagger} > 24$ kcal/mol. The ketonization barrier will be lower by the free-energy difference between tautomers in TCB. This difference can be estimated as 1 kcal/mol above the free energy of the enol's H-bond to Me_2SO,[17] the latter being approximately 4 kcal/mol.[10] Therefore the ketonization barrier for enol **2** is estimated as >19 kcal/mol under these conditions. This analysis, which estimates an apparent barrier for a pseudo-first-order process, indicates that enol **2** is probably isolable, especially under neutral conditions. A similar analysis should hold for enol **1**, and, since the rotational barrier for its keto form is higher than that for ketone **4**, the ketonization barrier should be correspondingly higher.[18]

Enol **1** was isolated in crystalline form by two methods: (a) neutralization of a solution of the enolate and (b) in vacuo concentration of a solution of the enol in liquid ammonia. That the compound is the enol tautomer was demonstrated by its acid-catalyzed conversion into ketone **3**. The NMR spectrum of the enol in Me_2SO-d_6 exhibits the hydroxyl proton absorption at δ 3.33, a value within the normal resonance range of an alcohol.[20]

There are three effects[21] which should be discussed as potentially important contributors to the stability of enols **1** and **2**; the sum of these contributions should equal 15–18 kcal/mol, the expected difference in bond energy[22] between tautomers. (a) The relaxation of strain favors the enol relative to the ketone. The ketone's rotational ground-state strain, which was observed above as the cause of the wide variation in rotational barriers, is relieved in the enol since the rotor's ortho sub-



ketone enol

stituents can straddle the planar acenaphthylenol ring system in an essentially strain-free manner. The major portion of the strain relieved in this process arises from the interaction of the inside rotor substituent and the π-electron cloud of the naphthalene nucleus. The resultant free-energy change should equal or exceed the 12 kcal/mol change observed when the phenyl group of ketone **7** is changed to a hydrogen atom (see above), especially since *both* the inside and outside interactions are relieved by the enolization process. (b) The variation of enol stability as a function of solvent reflects the effect of hydrogen bonding. The decrease in the K_{eq} from 2.6 in Me_2SO to ≤0.004 in hexane represents a free-energy change of at least 3.8 kcal/mol, which agrees with the free energy of H-bond complex formation for *p*-fluorophenol and Me_2SO.[10] (c) According to Craig's rules,[23] acenaphthylene is formally aromatic; thus, the acenaphthylenol system might be expected

to be resonance stabilized relative to the ketone. However, the acenaphthylene system is a nonalternant system, and as such the π-electron charge density distribution is uneven, and electrons of like spin can occupy adjacent carbons. Molecular orbital calculations[24] indicate that acenaphthylene is resonance stabilized by only 0.3 kcal/mol relative to naphthalene. Hückel molecular orbital calculations[25] indicate a slight *decrease* in resonance stabilization relative to naphthalene. ^{13}C NMR studies[26] suggest that acenaphthylene should be regarded as a naphthalene aromatic system which is only weakly coupled to a strongly localized double bond. Extensive chemical evidence[27] corroborates this conclusion. Resonance energy, therefore, does not appear to be an important factor contributing to the stability of the enols.

In conclusion, the relative thermodynamic stability of enols 1 and 2 is due principally to steric destabilization of the respective ketones. This effect is demonstrated by the increase in K_{eq} when Ar is changed from Mes to Tip while keeping the solvent constant. Comparable relative enol stability is not observed for 2-phenylacenaphthenone,[28] which lacks alkyl substituents on the rotor. An important consideration in the destabilization of 2-arylacenaphthenones is presumably the rigidity of the tricyclic ring system, which does not readily accommodate steric interactions by conformational mobility.[29]

Experimental Section[30]

2-Tipylacenaphthylenol (1). Method A. To a stirred ice-cold mixture of 0.5 g of sodium methoxide and 100 ml of dry THF under argon was added 1.0 g of ketone **3**. The royal-blue (i.e., a vivid, variable color between purple and blue) reaction mixture was stirred for 30 min at 0 °C and 45 min at room temperature, and was poured into 500 g of ice-cold 20% aqueous ammonium chloride. The orange oil was extracted into ether, and the ether layer was washed with ice water and worked up to give an orange paste, which crystallized from methanol–water. Recrystallization from methanol–water gave orange needles of enol **1**: mp 182–186 °C (red melt); the ir spectrum of the Nujol mull was identical with that of the enol as prepared by method B.

Method B. To 400 ml of distilled ammonia at the reflux temperature under argon was added dropwise over a period of 10 min a solution of 1.0 g of ketone **3** in 60 ml of dry THF, followed by 40 ml of dry ethyl ether. The resulting royal-blue solution was stirred at the reflux temperature for 1 h and was concentrated, with external heating, at aspirator pressure until a red color developed, and 400 ml of ice-cold saturated aqueous ammonium chloride was rapidly added. Work-up as for method A gave orange needles of enol **1**: ir (CCl_4) 3540, 1560, 1385, 1365 cm^{-1}; uv (Me_2SO) 438 nm (ϵ 770); NMR (Me_2SO-d_6) δ 1.02 (d), 1.15 (d, J = 7 Hz), 1.28 (d, J = 7 Hz), total preceding area 18 H, 3.03 (m, J = 7 Hz, total area 3 H), 3.33 (s, 1 H, OH), 6.80–7.96 (aromatic ring protons, total area 8 H); mass (12 eV) *m/e* (rel intensity) 370 (100), 328 (30), 327 (36), 286 (18), 285 (10), 203 (13). Anal. Calcd for $C_{27}H_{30}O$: C, 87.52; H, 8.16. Found: C, 87.61; H, 8.11.

Conversion of Enol 1 into Ketone 3. To a solution of 100 mg of the enol in 2 ml of glacial acetic acid at room temperature was added a few drops of 10% aqueous HCl. In a few minutes the color had faded to yellow and the reaction mixture was worked up to give, after evaporation of the pentane solvent, a white solid. The Nujol mull of this material exhibited an ir spectrum identical with that of ketone **3**.

1-Methoxy-2-mesitylacenaphthylene.[8] A royal-blue mixture of 0.3 g of ketone **4** and 0.05 g of pentane-washed NaH in 5 ml of dry THF at room temperature was allowed to stand until hydrogen evolution ceased, whereupon 0.5 ml of dimethyl sulfate was added. After 15 min, the reaction mixture was poured into water and extracted with benzene. The organic layer was washed with water and ammonia water, and was worked up to give an orange oil, which crystallized in the freezer. Recrystallization from methanol–water gave orange needles of the enol methyl ether: mp 115–116 °C (stable red melt); ir (CCl_4) 1625 (w), 1565, 1487, 1335 cm^{-1}; uv 205 nm (ϵ 72 000), 230 (58 000) 419 (880); NMR ($CDCl_3$) δ 2.23 (s, 6 H), 2.33 (s, 3 H), 3.73 (s, 3 H, OMe), 6.88–7.83 (aromatic ring protons, total area 8 H); mass (18 eV) *m/e* (rel intensity) 300 (100), 267 (16). Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.48; H, 6.80.

Enolates. The colors of the enolates of **1** and **2** were observed to vary as a function of counterion, the blue content diminishing in the order $K^+ > Na^+ > Li^+ \approx Mg^{2+}$. Dissociating solvents such as acetonitrile, acetone, and THF gave royal-blue solutions; alcohol solvents and benzene gave scarlet solutions. Addition of a few percent of THF to a scarlet benzene solution gave the royal-blue color. The enolates were insoluble in water. The potassium enolate of enol **2** was isolated as follows. To a solution of 0.5 g of ketone **4** in 50 ml of dry THF at room temperature under argon was added 0.5 g of heptane-washed potassium hydride. The royal-blue reaction mixture was stirred for 30 min and was filtered through a glass frit under an argon atmosphere. The solvent was evaporated in vacuo to give a deep purple solid. The ir spectrum (Nujol mull) exhibited no CO absorption but a weak absorption at 1640 cm^{-1}. The reddish solid sodium enolate was prepared analogously.

2-Phenyl-2-tipyl-1-acenaphthenone (7). A solution of 1.0 g of *trans*-1-phenyl-2-tipyl-1,2-acenaphthenediol (see below) and a catalytic amount of iodine in glacial acetic acid was refluxed a few minutes and worked up to give an oil, which crystallized from pentane to give 0.8 g of white material. Recrystallization from *n*-heptane gave pure ketone **7**: mp 167–169 °C; ir (CCl_4) 1726 cm^{-1}; uv 213 nm (ϵ 67 700), 253 (16 100), 318 (5700), 340 (5700); NMR ($CDCl_3$) δ 0.51 (d, J = 6.5 Hz, 6 H), 1.08–1.33 (three methyl lines, i.e., overlapping d, total area 12 H), 2.30–3.00 (superimposed m, total area 3 H), 7.00 (apparent singlet, area 7 H, phenyl protons superimposed upon tipyl ring protons), 7.56–8.17 (aromatic ring protons, total area 6 H); mass (18 eV) *m/e* (rel intensity) 446 (100), 403 (27). Anal. Calcd for $C_{33}H_{34}O$: C, 88.74; H, 7.67. Found: C, 88.81; H, 7.68.

***trans*-1-Phenyl-2-tipyl-1,2-acenaphthenediol.** To an ice-cold solution of phenyllithium (prepared from 15.7 g, 0.1 mol, of bromobenzene and 50 ml of ethyl ether) was rapidly added 5.8 g (15 mmol) of ketone **5** dissolved in 200 ml of benzene–ethyl ether (1:1 v/v) cooled to 0 °C. The mixture was vigorously stirred for 2 min and was worked up. The resulting oil was chromatographed on silica gel (eluted with benzene–cyclohexane, 1:1 v/v) to give 5 g of white solid, which was recrystallized from ethanol–water to give the pure diol: mp 171–173 °C; ir (CCl_4) 3596, 3534 cm^{-1}; uv 209 nm (ϵ 65 000), 228 (72 200), 292 (9300); NMR ($CDCl_3$) δ 0.72 (d, J = 6.5 Hz), 0.74 (d, J = 6.5 Hz), 1.00 (d, J = 6.5 Hz), 1.08 (d, J = 6.5 Hz), 1.28 (d, J = 7 Hz), total preceding area 18 H, 1.82–3.25 (two OH signals superimposed upon three methine signals, total area 5 H), 6.95–7.89 (aromatic ring protons, total area 13 H); NMR (CCl_4) a Varian T-60 spectrometer (probe temperature 30 °C) gave a spectrum exhibiting the OH signals as sharp singlets at δ 1.95 and 2.40; mass (18 eV) *m/e* (rel intensity) 464 (13), 421 (57), 231 (100). Discrete OH proton NMR signals indicate the trans configuration.[15] Anal. Calcd for $C_{33}H_{36}O_2$: C, 85.30; H, 7.81. Found: C, 85.41; H. 7.98.

5-Chloro-2-tipyl-1-acenaphthenone.[11] Dry hydrogen chloride was gently bubbled for 30 min through a stirred solution of 3.0 g of hydroxy ketone **5** in 60 ml of $CHCl_3$ at −10 °C. Stirring was continued for 2 h, after which dry nitrogen was bubbled through for 30 min and the yellow solution worked up to give a brown solid. This was washed with ice-cold 85% acetone to give 3.0 g of product, which was recrystallized thrice from acetone–water to give 2.0 g of near-white ketone: mp 197–199 °C; ir (CCl_4) 1727 cm^{-1}; uv 201 nm (ϵ 63 700), 218 (53 500), 256 (19 200), 323 (6100), 342 (5000); NMR ($CDCl_3$) δ 0.48 (d, J = 6.5 Hz, 3 H), 0.86 (d, J = 6.5 Hz, 3 H), 1.22–1.46 (overlapping methyl signals, total area 12 H), 1.76 (m, J = 6.5 Hz, 1 H), 2.69–3.48 (overlapping m, total area 2 H), 5.42 (broadened singlet, 1 H, H_2 enolizable proton, spin decoupling at 100 MHz indicates that this proton is coupled to the H_3 naphthalene ring proton, J = 1 Hz), 6.92–7.15 (complex m, tipyl ring protons superimposed on the H_3 ring proton, total area 3 H), 7.09 (d of doublets, J = 8 and 1 Hz, H_3 naphthalene ring proton),[15] 7.55 (d, J = 8 Hz, 1 H, H_4 naphthalene ring proton), 7.67–8.45 (m, H_6, H_7, and H_8 naphthalene ring protons, total area 3 H); mass (18 eV) *m/e* (rel intensity) 404 (100), 362 (25), 361 (52). Anal. Calcd for $C_{27}H_{29}ClO$: C, 80.08; H, 7.22; Cl, 8.76. Found: C, 79.81; H, 7.25; Cl, 8.75.

The rate of internal rotation as indicated by the line shape of the methyl proton region at 200 °C was identical with that for ketone **3**. This behavior is consistent with the structure assignment.

Equilibrium and Rate Measurements. Solvents were reagent grade. Monitoring of equilibration by the visible absorption spectrum employed the 440-nm band and concentrations of approximately 10^{-3} M. For the following conditions of solvent, equilibration time, and catalyst, equilibrium was approached from the ketone (visible absorption): EtOH, 30 h, piperidine catalyst; formic–acetic acid (1:2 v/v), 120 h, no catalyst; hexane, 12 h, piperidine catalyst; DMF, 30 h, no added catalyst. Equilibration of enol **1** in Me_2SO solution was monitored at 440 nm from the enol side under mineral acid catalysis and required 54 h. For enol **2** in Me_2SO-d_6 at a concentration of 0.5 M,

approach was from the keto side under CCl_3CO_2H catalysis for 24 h; K_{eq} was evaluated from the expression $K_{eq} = (m - n)/3n$ where m is the combined area of the enol methyl signals and the p-methyl signal of the ketone, and n is the area of the inside methyl signal of the ketone.

The rate constants for internal rotation under the conditions of Table I were as follows for each compound: **3,** $\leq 126\ s^{-1}$; **4,** $147\ s^{-1}$; **5,** $44\ s^{-1}$; **6,** $164\ s^{-1}$; **7,** $11\ s^{-1}$.

Mechanism of the Pinacol Rearrangement.[18] The intermediate deuterium-labeled diol, **2-tipyl-*trans*-1,2-acenaphthenediol-*1-d,*** was prepared analogously to the unlabeled diol[15] with $LiAlD_4$ replacing $LiAlH_4$. Recrystallization from n-heptane gave the deuterium-labeled diol: mp 177–179 °C; NMR (CCl_4) no detectable δ 5.46 signal.[15]

The rearrangement conditions were analogous to those for the preparation of ketone **3:** 0.6 g of the diol was dissolved in 4 ml of hot acetic acid, and 8 ml of hot formic acid was rapidly added, followed by addition of water to saturation. After crystallization commenced, the reaction mixture was cooled under tap water. The entire reaction procedure required approximately 2 min. The crystals were collected, washed with a minimum of chilled acetone–water, and dried in vacuo at 100 °C to give **2-tipyl-1-acenaphthenone-*2-d:*** NMR (CCl_4) as for ketone **3** except for δ 5.38 (s, $\leq$0.1 H).

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Registry No.—1, 59906-92-2; **2,** 59906-93-3; **2** methyl ether, 59906-94-4; **3,** 59261-58-4; **4,** 59261-56-2; **5,** 59261-61-9; **6,** 59261-60-8; **7,** 59906-95-5; *trans*-1-phenyl-2-tipyl-1,2-acenaphthenediol, 59906-96-6; 5-chloro-2-tipyl-1-acenaphthenone, 59906-97-7.

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(4) For a review of keto–enol tautomerism and the definition of "simple" enol, see G. H. Wheland, "Advanced Organic Chemistry", 3d ed, Wiley, New York, N.Y., 1960, p 663 ff.
(5) Reference 4, pp 677–678.
(6) R. C. Fuson, L. J. Armstrong, D. H. Chadwick, J. W. Kneisley, S. P. Rowland, W. J. Shenk, Jr., and Q. F. Soper, *J. Am. Chem. Soc.*, **67,** 386 (1945).
(7) I. A. Kaye, M. Fieser, and L. F. Fieser, *J. Am. Chem. Soc.*, **77,** 5936 (1955).
(8) (a) The enol acetate of 6-methyl-2-phenylacenaphthenone [J. W. Cook and R. A. E. Galley, *J. Chem. Soc.*, 2012 (1931)] is orange. (b) Likewise, the enol benzoate of 2-phenylacenaphthenone [C. F. Koelsch and H. J. Richter, *J. Am. Chem. Soc.*, **59,** 2165 (1937)] is orange; although Koelsch and Richter reported that they were unable to prepare the corresponding methyl ether, the methyl ether of enol **2** was readily prepared (see the Experimental Section).
(9) For thermodynamic studies of H-bond complexation with various nonhydroxylic bases, see ref 10. Absent by these methods (ir, NMR, calorimetry) are data for hydroxylic bases; in this regard, enol **1** as examined by the visible absorption spectrum could serve as a complementary probe of H-bond interactions.
(10) E. M. Arnett, E. J. Mitchell, and T. S. S. R. Murty, *J. Am. Chem. Soc.*, **96,** 3875 (1974).
(11) A halogenated derivative of ketone **3,** namely, 5-chloro-2-tipylacenaphthenone, has been prepared and its rotational barrier measured (see Experimental Section).
(12) (a) The "one-way" rate constant at coalescence is given by $k = \pi\Delta\nu/\sqrt{2}$ [F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, N.Y., 1969, pp 187–188]. (b) Previous studies [D. Y. Curtin, C. G. Carlson, and C. G. McCarty, *Can. J. Chem.*, **42,** 565 (1964)] have demonstrated that this method derives $\Delta G^{\ddagger}$ to within approximately 0.1 kcal/mol of the value derived by a more laborious, more rigorous graphical method.
(13) A. J. Gordon and R. A. Ford, "The Chemist's Companion", Wiley, New York, N.Y., 1972, p 136.
(14) For a discussion of analogous spectra, see ref 15. The spectrum of ketone **7** is an important anomaly. Since the outside isopropyl group also lies over an aromatic ring, the phenyl group, the absorption signals from both ortho groups occur upfield of the signals for the para group. The phenyl group in **7** also exhibits slow internal rotation at low temperature; for a discussion of the variable-temperature spectra of this highly hindered compound, see the thesis of A.R.M.
(15) A. R. Miller and D. Y. Curtin, *J. Am. Chem. Soc.*, **98,** 1860 (1976).
(16) This treatment assumes equienergetic activated complexes for a given rotor. The activated complex is analogous to that for the well-studied 9-arylfluorene system; for leading references, see W. T. Ford, T. B. Thompson, K. A. J. Snoble, and J. M. Timko, *J. Am. Chem. Soc.*, **97,** 95 (1975). In the fluorene system, the activated aryl group interacts with the C_1 and C_8 ring protons of the fluorene nucleus; in the 2-arylacenaphthenone system, the aryl group interacts in a geometrically analogous manner with the C_3 ring proton and a lone electron pair of the carbonyl group.
(17) The $K_{eq} = 0.3$ in Me_2SO-d_6 indicates that the enol is somewhat less than 1 kcal/mol above the ketone in energy. Presumably the diminution of the energy difference is due to the H-bonding to Me_2SO, the energy of which is gained by the enol in TCB solution.
(18) The enols would also be plausible low-energy intermediates in the "pinacol" rearrangement by which ketones **3** and **4** are prepared.[15] This hypothesis was tested by preparing the deuterium-labeled diol precursor which was then rearranged under normal reaction conditions (see Experimental Section). Since less than 10% protium was incorporated in the product ketone, despite the possibility of H/D exchange in the product, the enol mechanism[19] appears noncompetitive with the usual hydride shift mechanism.
(19) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1953, p 476.
(20) See, for example, J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds", Prentice-Hall, Englewood Cliffs, N.J., 1965, p 84.
(21) Two additional but probably less important effects favoring the enol are (a) increased entropy for the enol due to greater oscillatory freedom of the aryl group and (b) intramolecular H-bonding to the π-electron cloud of the rotationally locked aryl group.
(22) Reference 4, pp 695–696.
(23) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, N.Y., 1961, p 293.
(24) M. J. S. Dewar and C. deLlano, *J. Am. Chem. Soc.*, **91,** 789 (1969).
(25) B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **93,** 305 (1971).
(26) A. J. Jones, T. D. Alger, D. M. Grant, and W. M. Litchman, *J. Am. Chem. Soc.*, **92,** 2386 (1970).
(27) See, for example, M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85,** 2245 (1963).
(28) See ref 8b.
(29) A less rigid analogue of enol **2,** namely, the enol form of α-mesityldeoxybenzoin, in which the phenyl rings are not tied together, is reported[6] as being unstable; however, the equilibrium constant was not reported.
(30) The compounds not described below and other particulars have been previously reported.[15,31] The NMR and ir spectra, and the visible absorption spectra of enol **1** and the methyl ether of **2,** have been reproduced.[31]
(31) A. R. Miller, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1973, available from University Microfilms, Ann Arbor, Mich.