an unrelated development, we had an occasion to reinvestigate the experimental conditions for the hydroboration–oxidation of 2-methyl-2-butene with $BHBr_2{\cdot}SMe_2$ and correct the regiochemistry to 99.3:0.7 at the secondary and tertiary carbons, respectively.[19] The corrected regiochemistry does not call for an alternate mechanism at all. Our independent studies on the various dialkylborane dimers[20] and BH_3·Lewis base complexes[7] have shown that they dissociate prior to hydroboration as well. Thus, we are now convinced that the dissociation mechanism is generally applicable to all of the hydroborating agents.

Experimental Section

General procedures for the manipulation of boron reagents have been described.[21] All glassware, syringes, and needles were oven-dried at 140 °C for several hours. The glassware was assembled hot and cooled under a stream of dry nitrogen. Syringes were assembled and fitted with needles while hot and cooled as assembled units.

Materials. $BHBr_2{\cdot}SMe_2$ was prepared from $BH_3{\cdot}SMe_2$ and $BBr_3{\cdot}SMe_2$ by using a reported precedure[3] and was subsequently recrystallized[12] from CH_2Cl_2 at −78 °C. The alkenes were purified by distillation over LAH in a nitrogen atmosphere. The alkynes were purified by distillation in a nitrogen atmosphere. Me_2S was purified by distillation over 9-borabicyclo[3.3.1]nonane in nitrogen atmosphere. CH_2Cl_2 (Baker, analytical reagent grade) was stored over molecular sieves under nitrogen and used as such.

General Procedure for Kinetics Studies. The kinetics were studied by following the concentration of $BHBr_2{\cdot}SMe_2$ by measuring the absorbance of the B–H stretching vibration at 2500 cm^{-1} with Miran 1A variable filter infrared spectrometer from Wilks Scientific Corporation. A typical procedure is as follows. To a solution of Me_2S (4.85 mL of 0.515 M) in a 50-mL round-bottom flask were added $BHBr_2{\cdot}SMe_2$ in CH_2Cl_2 (1.56 mL, 1.60 M) and CH_2Cl_2 (18.28 mL). After equilibrating at 25.00 ± 0.05 °C (0.5 h), the solution was pumped through a 1-mm NaCl cell at a rate of 4 mL/min to measure the initial absorbance. The reaction was started by adding 1-hexene (0.313 mL) with the help of a syringe. The reactants and Me_2S were 0.100 M each. The absorbance was noted at desired time intervals. When the reactions were sufficiently fast, the absorbance was continuously recorded on a chart paper. On the other hand, when they were slow, the absorbances were noted at some specific time intervals alone. The background absorbance was measured by pumping pure CH_2Cl_2 through the cell. The absorbances were translated into concentrations, and the rate constants were obtained by procedures already published.[13] The rate studies (Figure 1) were also made by the quantitative IR procedure.

Hydroboration of Alkenes with $BHBr_2{\cdot}SMe_2$ in the Presence of Catalytic Amounts of Boron Tribromide. The following procedure is representative. To 2.60 mL of $Br_2BH{\cdot}SMe_2$ in CH_2Cl_2 (1.84 M), *n*-octane (0.3 mL) (internal standard), and CH_2Cl_2 (0.3 mL) was added cyclohexene (0.55 mL, 10% excess). Then BBr_3 (1.0 mL of a 0.5 M solution of CH_2Cl_2) was added dropwise while the reaction mixture was cooled with ice. After being stirred for about 10 min, the reaction mixture was then refluxed. After 6 h, the ^{11}B NMR showed that the reaction is complete. Oxidation with alkaline H_2O_2 and analysis by GC indicated that cyclohexanol was formed in 97% yield.

Acknowledgment. Financial support from the National Science Foundation (Grant CHE 79-18881) is gratefully acknowledged.

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Association of α-Alkyl-β,β-dimesitylethenols with Hydrogen Bond Accepting Solvents[1]

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Received March 15, 1988

The δ(OH) values for α-alkyl-β,β-dimesitylethenols ($Mes_2C{=}C(OH)R$, **2**, R = Me, Et, *i*-Pr, *t*-Bu) were measured in eight solvents and in several binary CCl_4–DMSO-d_6 mixtures. Large shifts to a lower field were observed on increasing the hydrogen bond accepting ability of the solvent or the mixture. The δ(OH) value for **2** in the various solvents were linear with δ(OH) for $Mes_2C{=}CHOH$ (**1**) and approximately linear (with slopes C) with Kamlet–Taft's hydrogen bond accepting parameter β of the solvent. Long-range couplings ^4J(HCCOH) were observed for **2**, *R* = *i*-Pr in several solvents but not in DMSO. The change in δ(OH) in the CCl_4–DMSO-d_6 mixtures was analyzed in terms of formation of a 1:1 association complex of the enol with DMSO and assuming that a syn-type conformer in CCl_4 and an anti-type conformer in DMSO are present in a rapid equilibrium. The δ(OH) for the anti-type conformer ($\delta_{anti{\cdot}DMSO}$) was calculated, but information on its exact geometry is not available. Complete association with DMSO is not achieved even in the pure solvent. The log K_{assoc} values are linearly correlated with the σ^* values and decrease nonlinearly with the increase in the steric parameter E_s. They are linear with the slopes *C* and with $\delta_{anti{\cdot}DMSO}$. The polar effect on K_{assoc} is in the expected direction. The small sensitivity to steric effects is in contrast with the large sensitivity to steric effects found for other mechanistic phenomena on increasing the bulk of R in **1** and **2**. This is presumably due to the occurrence of the association with the hydrogen bond accepting solvent on the relatively unhindered side of the crowded enol molecules.

The conformation of the C=COH moiety and the interaction of the OH group of stable simple enols with hydrogen bond accepting solvents was previously investigated by IR and NMR techniques for several β,β-dimesityl-α-aryl- (and α-H) ethenols.[2] The most extensively studied compound was 2,2-dimesitylethenol (**1**) for which it was concluded from the changes of the coupling constant ^3J(HCOH) and the chemical shift of the enolic proton δ(OH) with the solvent that the conformation of the C=COH moiety around the C–O bond is syn planar (**1a**)

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[1] Part 20 is in the series "Stable Simple Enols". For part 19, see Biali, S. E.; Nugiel, D. A.; Rappoport, Z., submitted to *J. Am. Chem. Soc.* for publication.

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Table I. δ(OH) Values for Enols 2 and ^4J(HCCOH) in Several Solvents at 296 K

			δ(OH) in					
no.	solvent	β^a	**1**^{b}	**2a**	**2b**	**2c**	**2d**	^4J(HCCOH) (**2c**)
1	CCl_4	0	4.74	4.74	4.74	4.67	4.77	1.57
2	$C_6D_5CD_3$	0.10	4.30	4.76	4.79	4.70	4.80	1.56
3	$CDCl_3$	0	4.66	4.97	4.92	4.83	4.88	1.57^c
4	CD_3CN	0.31	6.22	5.74	5.69	5.53	5.53	1.56
5	CD_3COCD_3	0.48	7.65 8.84^d	6.88 7.93^d	6.73 7.81^d	6.50 7.44^d	6.38 7.37^d	1.62
6	THF-d_8	0.55	7.51	6.87	6.84	6.59	6.50	1.61
7	DMSO-d_6	0.76	9.01	8.21	8.00	7.60	7.30	0^d
8	DMF-d_7	0.69	9.17	8.29	8.21	8.02	7.81	0^d

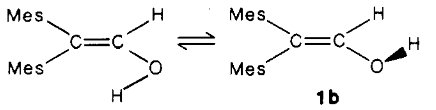
^{a} From ref 3. ^{b} From ref 2. ^{c} Also in CD_2Cl_2. ^{d} At 190 K.

Table II. Parameters of the Correlations of Eq 2 and 3 in Eight Solvents

R	A	B	R^a	SD^b	C	D	R^a	SD^b
H^c					6.36	4.34	0.980	0.37
Me	0.74	1.35	0.9930	0.16	4.74	4.59	0.9772	0.29
Et	0.71	1.49	0.9919	0.17	4.56	4.59	0.9777	0.28
i-Pr	0.67	1.62	0.9895	0.18	4.24	4.52	0.9704	0.30
t-Bu	0.60	2.04	0.9871	0.18	3.77	4.63	0.9672	0.28
Mes^c	0.69	1.84	0.9870	0.19	4.47	4.83	0.974	0.31
Ph^c	0.77	1.52	0.9950	0.13	4.98	4.84	0.981	0.29
9-anthryl^c	0.81	1.74	0.9855	0.24	5.20	5.26	0.968	0.39

^{a} Correlation coefficient. ^{b} Standard deviation. ^{c} Data from ref 2 in 12 or 13 solvents.

in non-hydrogen bonding accepting solvents, e.g., CCl_4, and is anti clinal (**1b**) in strong hydrogen bond accepting solvents, e.g., DMSO, and that both conformations coexist with appreciable populations in a rapid equilibrium in moderate hydrogen bond accepting solvents (eq 1). A combination of IR measurements, analysis of the solvent dependence of the chemical shifts and coupling constants by Kamlet–Taft solvatochromic relationships,[3] and the δ(OH) dependence of β-Mes-Me-d_9 *E*/*Z* isotopomeric trimesitylethenols as a function of the solvent indicated the interactions responsible for the solvent-dependent conformation.[2] The apparently more crowded conformer **1a** gains some stability from hydrogen bonding between the OH and the mesityl group cis to it [π(Ar)–HO], whereas in hydrogen bond accepting solvents the stronger interaction of the OH with the solvent S, COH···S stabilizes the conformation in which the arrangement of the OH group is optimal for intermolecular hydrogen bond (**1b**). These results somewhat differ from those of Capon and co-workers[4] who concluded from ^3J(HCOH) and ^4J(HCCOH) values in >99.5% acetone that vinyl alcohol and (*E*)-1-propenol exist predominantly in the syn arrangement, while (*Z*)-1-propenol and 2-methyl-1-propen-1-ol are predominantly in the anti conformation. Steric effects were invoked to explain this behavior. However, ab initio molecular orbital (MO) calculations indicate that in the gas phase the preferred conformation of the above compounds is syn.[5]



1a **1b**

Mes = mesityl = 2,4,6-$Me_3C_6H_2$

(1)

The number of solvent molecules associated with the OH in conformation **1b** and the corresponding association constant K_{assoc} were obtained from analysis of the change in both δ(OH) and ^3J(HCOH) for **1** in CCl_4–DMSO-d_6 mixtures.[2] It was concluded that only a single DMSO molecule is associated with **1b**, and the K_{assoc} values based on ^3J(HCOH) and δ(OH) differed by 15%, being 9.35 and 7.9, respectively, in spite of the fact that the values were derived from data in somewhat different ranges of binary CCl_4–DMSO-d_6 mixtures.[2]

Recent studies indicated the importance of steric effects of α-substituents on the relative stability,[6] rotational barriers,[4,7] and structural parameters[8] of α-alkyl- (and α-H) β,β-dimesitylethenols. It was therefore of interest to investigate the effect of α-alkyl substituents on the association with the solvent.

The change in the substituent at the α-position of β,β-dimesityl-α-alkylethenols (**2**) involved the classical series of alkyl substituents Me, Et, *i*-Pr, and *t*-Bu. The solvent chosen for the association studies was DMSO, an excellent hydrogen bond accepting solvent that enables comparison with previous studies with **1**,[2] and other solvents were studied briefly.

$$Mes_2C{=}C(OH)R$$

2a: R = Me
2b: R = Et
2c: R = *i*-Pr
2d: R = *t*-Bu

Results

Enols **2a–d** were synthesized as described previously.[6] Their δ(OH) values were measured in several pure solvents as well as in binary CCl_4–DMSO-d_6 mixtures.

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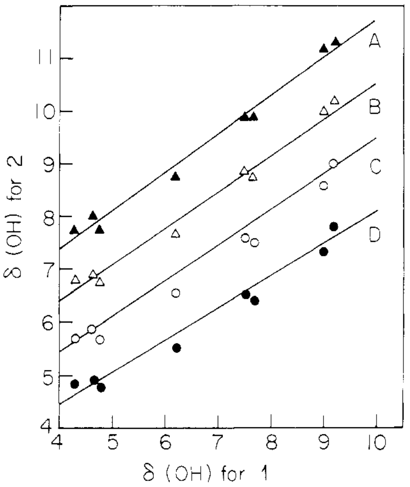

Figure 1. Plots of δ(OH) for compounds **2** vs δ(OH) for **1** in different solvents. (A) δ(OH) + 3 for **2a** (▲). (B) δ(OH) + 2 for **2b** (△). (C) δ(OH) + 1 for **2c** (○). (D) δ(OH) for **2d** (●).

δ(OH) in Pure Solvents. The ^{1}H NMR spectra of the enols **2** (200 MHz, room temperature) were measured in eight solvents that differ in their polarity and hydrogen bond accepting ability. In all cases broadening of the methyl and aromatic proton signals was observed[9] and their chemical shifts were rather insensitive to the solvent. In contrast, the OH signals were sharp and the δ(OH) was strongly solvent dependent (Table I). The effects of the solvent change on δ(OH) are proportional for the various enols and plots of δ(OH) for **2a–d** vs δ(OH) for **1** are all linear ($R \geq 0.985$) (Figure 1). The parameters of eq 2 are

$$\delta(\mathrm{OH})[\mathbf{2}] = A\delta(\mathrm{OH})[\mathbf{1}] + B \qquad (2)$$

given in Table II together with previous data for comparison. Table II shows that for **2a–d** the sensitivity of δ(OH) to the change of solvent (i.e., A) decreases with the increased bulk of the substituent. Although the large standard deviations of the lines seem to detract from this conclusion, we believe that this trend is valid since all the lines in Figure 1 show a similar scatter of the points. The δ(OH) values are also temperature-dependent and δ(OH) values of **2a–d** in CD_3COCD_3 increase by 0.96–1.19 ppm on decreasing the temperature from 296 K to 190 K (Table I). In $C_6D_5CD_3$ δ(OH) for **2a** changes from 4.76 at 296 K to 4.84 at 200 K.

The δ(OH) values for each enol were also plotted against Kamlet–Taft's solvatochromic parameters β of the solvents[3] (Figure 2). Approximate linear relationships (eq 3) with similar shapes and deviations for all the enols were observed. The parameters of eq 3 are given in Table II.

$$\delta(\mathrm{OH})[\mathrm{Mes_2C{=}C(OH)R}] = C\beta + D \qquad (3)$$

Long-range coupling of the OH proton (^4J(HCCOH)) with protons on C_α of the alkyl group was also observed. Such coupling is absent for **2d**, which lacks C_α-hydrogens, whereas for **2b** it is not seen due to overlap of signals. For **2a** two ^4J(HCCOH) values were measured: 1.18 Hz in $CDCl_3$ and 0.86 Hz in $C_6D_5CD_3$. For **2c** the OH splitting to a doublet in different solvents gave the ^4J(HCCOH) coupling constants, which are given in Table I. These values are nearly constant in all the solvents except DMF-d_7 and DMSO-d_6, where the OH appears as a broad singlet and the CH group appears as a single septet.

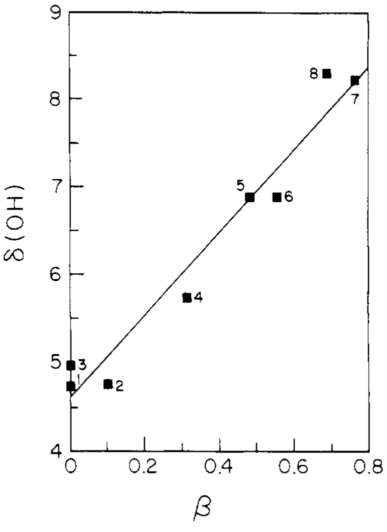

Figure 2. Plot of δ(OH) values for **2a** vs Kamlet–Taft's β parameter. The numbering of the points is according to Table I.

Table III. δ(OH) Values for $Mes_2C{=}C(OH)R$ in CCl_4–DMSO-d_6 Mixtures at 296 K[a]

% DMSO-d_6 in CCl_4 (v/v)	DMSO-d_6, M	R			
		Me	Et	*i*-Pr	*t*-Bu
0	0	4.74	4.74	4.67[b]	4.77
5	0.71	6.63	6.33	5.74[c]	5.60
6.6	0.92			5.97[d]	
8	1.13	7.01	6.65	6.07[e]	5.84
12.6	1.78	7.29	6.94	6.45[e]	5.96
20	2.83	7.54	7.22	6.75[e]	6.33
100	14.14	8.21	8.00	7.60[e]	7.30

[a] [enol] = 0.0417 M. [b] ^4J(HCCOH) = 1.57 Hz. [c] ^4J(HCCOH) = 1.46 Hz. [d] ^4J(HCCOH) = 1.34 Hz. [e] Coupling was not observed within the experimental error.

δ(OH) in Binary CCl_4–DMSO-d_6 Mixtures. The δ(OH) values for **2a–d** in pure CCl_4 and DMSO-d_6 and in four to five of their binary mixtures up to 20% (v/v) DMSO-d_6 in CCl_4 were determined. With **2a** and **2b** half of the change in δ(OH) was already achieved on addition of 5% DMSO, whereas with **2c** and **2d** higher percentages of DMSO were required (Table III). The δ(OH) in CCl_4 was nearly the same for **2a–d** (but higher than that for **1**), and the bulkier the alkyl group, the smaller the shift of δ(OH) in DMSO-d_6.

The plot of δ(OH) for **2b** vs δ(OH) of **2a** is linear with a slope of 0.9. Similar plots for **2c** and **2d** are curved, i.e., on increasing the percentage of DMSO, the change in δ(OH) for **2a** approaches a plateau at high [DMSO] whereas the change in the δ(OH) for **2c** and **2d** is still appreciable.

The ^4J(HCCOH) coupling constants for **2c** (footnotes to Table III) decrease slowly on increasing the percentage of DMSO up to 6.6%, but at higher percentages no coupling was observed.

Calculation of K_{assoc}. For calculation of K_{assoc} (eq 4) we showed previously[2] that a plot of K, the equilibrium constant for eq 1, vs the [DMSO] which is not associated with the anti conformer ($[\mathrm{DMSO}]_f$), is linear with a slope of K_{assoc} (eq 5).

$$\text{syn} + \text{DMSO} \xrightleftharpoons{K_{assoc}} \text{anti·DMSO} \qquad (4)$$

$$K_{assoc} = [\text{anti·DMSO}]/([\text{syn}][\text{DMSO}]_f) = K/[\text{DMSO}]_f \qquad (5)$$

The ratio between the associated and the nonassociated enol can be calculated from δ(OH) by using the assumptions that the interconversion of the two conformers is a fast process on the NMR time scale and that the solvent effect on δ(OH) of each conformer is small. The observed

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[9] The associated dynamic process is discussed in ref 1.

Table IV. K_{assoc} **and** $\delta_{anti\cdot DMSO}$ **Values for** $Mes_2C{=}C(OH)R$ **in Binary** CCl_4**–DMSO-**d_6 **Mixtures at 296 K**

parameter	R: H	Me	Et	*i*-Pr	*t*-Bu
$K_{assoc}{}^{app\,a}$	7.9[b]	1.48	1.19	0.88	0.55
δ_{DMSO}	9.01	8.21	8.00	7.60	7.30
$K_{assoc}{}^{c}$	5.25	1.38	1.04	0.70	0.47
R^d	0.9997	0.9999	0.9998	0.9999	0.9983
SD[d]	0.001	0.002	0.003	0.002	0.012
$\delta_{anti\cdot DMSO}{}^{c}$	9.01	8.38	8.25	7.89	7.67
$F_{anti\cdot DMSO}$ in DMSO[e]	1.0	0.95	0.93	0.915	0.87

[a] From eq 5, assuming that $\delta_{anti\cdot DMSO} = \delta_{DMSO}$. [b] From ref 2. [c] From the iterative treatment of eq 9. [d] R = correlation coefficient; SD = standard deviation of the plots according to eq 9. [e] From $(\delta_{DMSO} - \delta_{CCl_4})/(\delta_{anti\cdot DMSO} - \delta_{CCl_4})$.

δ(OH) value in the CCl_4–DMSO mixture (δ_{obsd}) will then be a weighted average of the δ values for pure species, i.e., δ(syn) and δ(anti·DMSO), each multiplied by its mole fraction F. When $F_{anti\cdot DMSO}$ is the fraction of the complexed conformer eq 6 is obtained.

$$\delta_{obsd} = \delta_{syn}(1 - F_{anti\cdot DMSO}) + \delta_{anti\cdot DMSO}\, F_{anti\cdot DMSO} \quad (6)$$

By inserting $[enol]_0 = [syn] + [anti\cdot DMSO]$, eq 7 and 8 are obtained. There are three unknowns in these

$$\delta_{obsd} = \delta_{syn}([enol]_0 - [anti\cdot DMSO])/[enol]_0 + \delta_{anti\cdot DMSO}([anti\cdot DMSO]/[enol]_0) \quad (7)$$

$$[anti\cdot DMSO] = ((\delta_{obsd} - \delta_{syn})/(\delta_{anti\cdot DMSO} - \delta_{syn}))[enol]_0 \quad (8)$$

equations, K_{assoc}, δ_{syn} and $\delta_{anti\cdot DMSO}$ and the two δ values should be estimated in order to obtain K_{assoc}. The assumption that $\delta_{syn} \approx \delta_{CCl_4}$ is justified since (a) no association with CCl_4 is expected as $\beta(CCl_4)$ has the lowest possible β value of 0,[3] (b) the IR spectra show ≥98% of internally (OH)-π-(*cis*-Mes) associated conformer for 1,[2,10] and (c) the δ(OH) values are nearly structure-independent in CCl_4. However, in contrast with the case of 1 there is no evidence that in DMSO only the anti·DMSO conformer is present. Using this assumption and eq 5 and 8, we calculated apparent K_{assoc} values ($K_{assoc}{}^{app}$) since it is interesting to what extent the assumption affects the calculated value of K_{assoc}.

Rearrangement of eq 7 after insertion of eq 5 gave eq 9 where $[DMSO]_0$ is the DMSO added at each CCl_4–DMSO-d_6 mixture. A plot of the experimentally known

$$[DMSO]_0/(\delta_{obsd} - \delta_{CCl_4}) = ([enol]_0 + [DMSO]_0 - [anti\cdot DMSO])/(\delta_{anti\cdot DMSO} - \delta_{CCl_4}) + 1/K_{assoc}(\delta_{anti\cdot DMSO} - \delta_{CCl_4}) \quad (9)$$

left side of eq 9 against $([enol]_0 + [DMSO]_0 - [anti\cdot DMSO])$ should be linear with a slope of $1/(\delta_{anti\cdot DMSO} - \delta_{CCl_4})$ and an intercept of $1/K_{assoc}(\delta_{anti\cdot DMSO} - \delta_{CCl_4})$.

The [anti·DMSO] value is unknown, and therefore the $[enol]_0/(\delta_{obsd} - \delta_{CCl_4})$ values were plotted against $[enol]_0 + [DMSO]_0$ values. The obtained slope was then used to calculate the [anti·DMSO] value by eq 8, and this value was then used in another iteration of eq 9. Since $[anti\cdot DMSO] \ll [DMSO]_0$ for almost all points, only one iteration was sufficient to obtain convergent $\delta_{anti\cdot DMSO}$ and K_{assoc} values. This treatment[11a] or a variation on it resembles the simultaneous calculation of the K_{assoc} and ϵ for 1:1 charge transfer complexes by the Benesi–Hildebrand equation.[12a] The errors associated with this equation[12b] and the validity of the assumptions and the errors in the NMR method were discussed extensively.[13] The $K_{assoc}{}^{app}$, K_{assoc}, and $\delta_{anti\cdot DMSO}$ values, the calculated fraction of the anti conformer in DMSO, and the parameters of the plots are given in Table IV. The linearity of the plots of eq 9 is demonstrated in Figure S1 in the supplementary material.

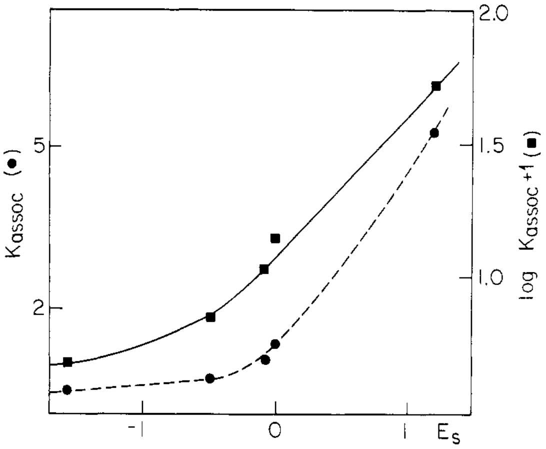

Figure 3. Plots of K_{assoc} in DMSO (●, full line) and log K_{assoc} + 1 (■, broken line) for enols **2a–d** vs Taft's E_s values.

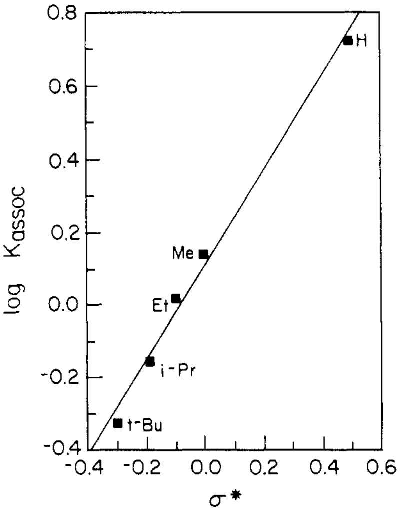

Figure 4. A plot of log K_{assoc} for enols **1**, **2a–d** vs Taft's σ^* values.

The assumption that only the anti conformer is present in pure DMSO is correct for 1 but not for the α-alkyl-substituted enols (Table IV). The fraction of this conformer which is ≥87% for **2a–d**, decreases with the increased bulk of R. For **2a–d**, K_{assoc} is between 7 and 20% smaller than $K_{assoc}{}^{app}$.

Correlations Involving K_{assoc}**.** The K_{assoc} values for 2 (Table IV) are much smaller than the value obtained previously for 1, and they decrease with the increase of the bulk of R. Calculation of K_{assoc} for 1 by eq 9 gave a value which is only 2/3 of the value calculated previously,[2] and a somewhat higher value is obtained by another calculation technique. The reason for this will be discussed else-

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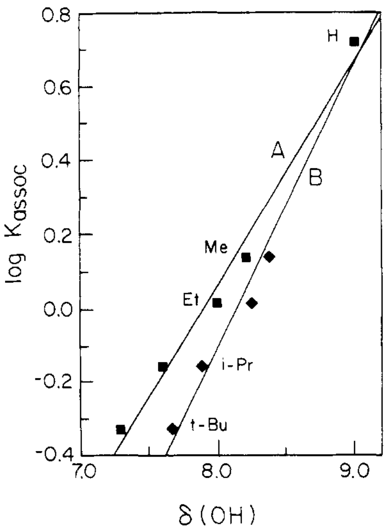

Figure 5. A plot of log K_{assoc} vs δ(OH): (A) vs δ_{DMSO} (■); (B) vs $\delta_{\text{anti·DMSO}}$ (●).

where.[14] Due to the linearity observed between solid-state bond and torsional angles,[8] rotational barriers,[1] $\Delta G°$ values for the keto ⇌ enol equilibria,[6] and Taft's steric parameter E_s[15a] of substituent R in 1 and 2, correlations between K_{assoc} or log K_{assoc} and E_s values were attempted. Such correlations are nonlinear, and although the correlation coefficient for the log K_{assoc} plot is 0.96, a curve gives a better fit to the data (Figure 3). A correlation of log K_{assoc} with Taft's σ^* value[15b] is linear as shown in Figure 4 (eq 10).[16]

$$\log K_{\text{assoc}} = 1.30\sigma^* + 0.10 \quad (R = 0.9957,\ \text{SD} = 0.07) \qquad (10)$$

A plot of K_{assoc} values vs the slopes C of the correlation of eq 3, taken from Table II, shows a spread of the points. However, a plot of the log K_{assoc} values vs C is linear (Figure S2 in the supplementary material), according to eq 11.

$$\log K_{\text{assoc}} = 0.41C - 1.84 \quad (R = 0.9959,\ \text{SD} = 0.02) \qquad (11)$$

Relationships Involving δ(OH) Values. The measured δ(OH) in DMSO (δ_{DMSO}) and the calculated δ(OH) for the anti conformation in DMSO ($\delta_{\text{anti·DMSO}}$) are linearly correlated according to eq 12. Consequently, the quality of correlations involving δ_{DMSO} or $\delta_{\text{anti·DMSO}}$ will be the same, although they will have different slopes.

$$\delta_{\text{anti·DMSO}} = 0.79\delta_{\text{DMSO}} + 1.92 \quad (R = 0.9995,\ \text{SD} = 0.01) \qquad (12)$$

Plots of log K_{assoc} against either the experimentally measured δ_{DMSO} or the calculated $\delta_{\text{anti·DMSO}}$ are linear (Figure 5) with the parameters of eq 13 and 14. Interestingly, a plot of K_{assoc} vs $\delta_{\text{anti·DMSO}}$ for enols 2 is also approximately linear (eq 15).

$$\log K_{\text{assoc}} = 0.61\delta_{\text{DMSO}} - 4.8 \quad (R = 0.9934,\ \text{SD} = 0.04) \qquad (13)$$

$$\log K_{\text{assoc}} = 0.77\delta_{\text{anti·DMSO}} - 6.3 \quad (R = 0.9909,\ \text{SD} = 0.06) \qquad (14)$$

$$K_{\text{assoc}} = 1.20\ \delta_{\text{anti·DMSO}} - 8.7 \quad (R = 0.9811,\ \text{SD} = 0.17) \qquad (15)$$

Approximate linear relationships were found when δ_{DMSO} and $\delta_{\text{anti·DMSO}}$ values were correlated with the σ^* and E_s values (eq 16–19).

$$\delta_{\text{DMSO}} = 2.09\ \sigma^* + 8.1 \quad (R = 0.9788,\ \text{SD} = 0.25) \qquad (16)$$

$$\delta_{\text{anti·DMSO}} = 1.64\sigma^* + 8.3 \quad (R = 0.9746,\ \text{SD} = 0.22) \qquad (17)$$

$$\delta_{\text{DMSO}} = 0.63E_s + 8.1 \quad (R = 0.9710,\ \text{SD} = 0.09) \qquad (18)$$

$$\delta_{\text{anti·DMSO}} = 0.5E_s + 8.3 \quad (R = 0.9703,\ \text{SD} = 0.07) \qquad (19)$$

IR Spectra. The IR spectra of **1** and **2d** in DMSO-d_6 and of **1** in CCl_4 were measured. The main absorption of **2d** in CCl_4 in the OH region is a sharp peak at 3529 cm^{-1}, at almost the same position as that for **1**.[2] In DMSO-d_6 broad absorptions around 3500 cm^{-1} and a fine structure of several peaks at 3251–3275 cm^{-1} for both compounds were observed.

Discussion

Interaction of the OH Group with the Solvent. The major conclusion from the data of Table I and the linear δ(OH) vs β correlation (Figure 2) is that the large shifts in δ(OH) with the change of the solvent from CCl_4 are due to association of the OH with the hydrogen bond accepting solvent. In analogy with the behavior of **1** (cf. Figure 1), we believe that the association is accompanied by a conformational change to a solvated anti-type conformation and that the two conformers interconvert rapidly. The detailed geometries of the anti-type conformations in the different solvents are not necessarily the same. Hence the conformers' equilibria are better probed in a binary solvent mixture where it is assumed that the solvent effect on the conformers' geometry is negligible in the entire solvent range.

Conformational Equilibria in CCl_4–DMSO-d_6 Mixtures. The choice of CCl_4–DMSO-d_6 mixtures for studying the α-substituent effect on the association of the OH group with the solvent is based on several considerations. DMSO has the highest β value of all our solvents and it causes the largest shifts of δ(OH). Also the K_{assoc} value for **1** in DMSO is the highest of the values in several solvents.[14] Moreover, the changes in δ(OH) and in ^3J(HCOH) for **1** are parallel,[2] and since the analysis of ^3J(HCOH) values suggests that in DMSO-d_6 the conformation is exclusively of the anti-type, and the OH is strongly hydrogen bonded to the solvent, high δ(OH) values for other enols presumably indicate the formation of similar anti-type conformations.

The appearance of an OH absorption with ≥98% of the intensity of $\sum\nu_{\text{OH}}$ in the IR spectra of **1** and **2d** (the enols with the larger and smaller R's) in CCl_4 at 3529 cm^{-1} shows the nearly exclusive presence of a hydrogen-bonded conformation. The sharpness of the peak, the low hydrogen bond accepting ability of CCl_4, and analogy with **1** suggest that this is an intramolecularly bonded (presumably syn) conformation. The main absorptions at 3251–3275 cm^{-1} in DMSO-d_6 indicate a much stronger hydrogen bonding, presumably with the DMSO. Since the broad peak in DMSO may be due to traces of water, we cannot decide whether an absorption at 3529 cm^{-1} for **2d** in DMSO is present. The presence of both conformers for **2a–d** in DMSO is deduced from the NMR spectral data. As shown in Table III, even though addition of only 5% v/v of DMSO to CCl_4 causes ca. half and one-third of the change in δ(OH) for **2a**, **2b** and for **2c** and **2d**, respectively, the percentage of the anti·DMSO conformation in pure DMSO is still 87–95% (Table IV). Consequently, in spite of the good linearity obtained in calculating $K_{\text{assoc}}^{\text{app}}$ values, they

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[14] Nadler, E. B.; Rappoport, Z., unpublished results.

[15] (a) Taft, R. W., Jr. *J. Am. Chem. Soc.* **1953**, *75*, 4538. (b) Taft, R. W., Jr. *Ibid.* **1952**, *74*, 2729.

[16] A similar correlation with the σ_I values recommended by Exner[17] gave the correlation log $K_{\text{assoc}} = 14.6\sigma_I + 0.75$ ($R = 0.9848$, SD = 1.48). However, since Exner's σ_I values for the alkyl groups differ very slightly and their scale is much compressed compared to that of the σ^*, only the correlation with σ^* is presented.

[17] Exner, O. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum: New York, 1978; Chapter 10, p 438.

can differ from the "true" K_{assoc} values. Moreover, the linearity of δ(OH)[2] with δ(OH)[1] (Figure 1) cannot be taken as evidence for the exclusive presence of an anti conformation in DMSO.

Effects of Structural Parameters on K_{assoc} Values. A priori, α-alkyl substituents should affect the strength of the hydrogen-bonding interaction involving the OH group both electronically and sterically. Two important results are deduced from Table IV. First, the change caused by the α-alkyl (or H) substituent on K_{assoc} is smaller than changes caused by the same substituents on structural, dynamic, and thermodynamic parameters of compounds **1** and **2**.[1,6,8] For the changes R = H → R = *t*-Bu and R = H → R = Me, K_{assoc} changes by 11- and 2.9-fold, repectively.

Second, the better linearity of the log K_{assoc} vs σ* plot (Figure 4) compared with the log K_{assoc} vs E_s plot (Figure 3) suggest that the effect of the change of R on K_{assoc} is mainly electronic and not steric. However, since the inductive effects of alkyl groups are frequently regarded as identical[18] and the σ* values may still contain residual steric effects, the linearity of Figure 4 may be fortuitous. An argument for the relatively low importance of steric effects is the near additivity of the effect of added methyl groups at the α-substituent on K_{assoc}. This is in contrast to the expected "telescopic" decrease in K_{assoc}, either for the change from α-Et or from α-*i*-Pr to α-*t*-Bu (see below) if the steric factor predominates. The ρ* value of 1.30 for **2** is reminiscent of the increase of K_{assoc} by a polar effect as shown by the linear correlation of log K_{assoc} vs Hammett's σ (ρ = 0.35) for *m*- and *p*-substituted α-aryl-β,β-dimesitylethenols.[14]

The hydrogen bond donor ability of the OH in both the intramolecular and the intermolecular hydrogen bonded conformations should decrease by electron donation. The decrease of both K_{assoc} and $\delta_{anti \cdot DMSO}$ with the increased electron donation by R (Figure 5) could be explained if the field effect component of the polar effect is more pronounced in the anti-type conformation due to the vicinity of the α-R and the OH dipoles.

The increased bulk of α-R will not affect directly the stability of the syn conformer since it is remote from the OH. However, it will reduce the stability of the anti-type conformation by steric interaction with the OH group, and by partially occupying the position to be held by the solvating DMSO molecule.

The solid-state structure[8] and molecular mechanics (MM) calculations show that in the stable conformation a C–H bond of R in **2a**, **2b**, and **2c**, or a C–C bond in **2d** nearly eclipses the C=C bond. Consequently, the approximate steric environment on the side of the alkyl group remote from the double bond and close to the OH group is similar in the anti·DMSO conformers of **2c** and **2d**. Moreover, if the conformation in which the smaller hydrogen is placed near the OH group of **2b** is the most stable, it will be approximately similar to the conformation of **2a** at the association site if the changes in the R–C–O bond angle caused by R are neglected. However, the consequent expected large difference in K_{assoc} between **2b** (R = Et) and **2c** (R = *i*-Pr) is not observed. The higher K_{assoc} for **1** than for **2a–d** can be partially due to unhindered solvation of the unencumbered OH by the DMSO.

Consequently, electronic and steric effects seem to reinforce each other in slightly decreasing K_{assoc} with the increased bulk of R. The overall low sensitivity to steric effects in interesting since the magnitude of phenomena associated with the C_β ring cis to R, like mesityl rotational barriers,[1] steric isotope effect,[19] bond and torsional angles,[8] and presumably keto ⇌ enol equilibria[6] is predominated by steric effects. In contrast, for phenomena occurring at the other side of the double bond, like the association with DMSO, the steric effects are relatively minor in spite of the geometrical constraints caused by the double bond.

Comparison with Other Alcohol Systems. Our enols are monomeric even in CCl_4, due to both the intramolecular OH···π(*cis*-Mes) association and to steric effects that inhibit mutual approach of two crowded enol molecules. The evidence is the appearance of two separate OH signals for a mixture of the *E* and *Z* isotopomeric enols Mes*C(Mes)=C(OH)R, Mes* = 2,4,6-$(CD_3)_3C_6H_2$, R = H, Mes, Mes*,[19] as well as the low dependence on concentration of δ(OH) for **1**.[14] Consequently, our K_{assoc} values relate to "monomeric" enols. This is of interest since a recent analysis showed that "monomeric" and "oligomeric" alcohols differ in their abilities as hydrogen-bond acceptors.[20]

For comparison of our K_{assoc} values we searched in ref 11b, which covers the 1960–1973 period for data on systems RCOH, which are the closest analogues to our system, as well as for ROH systems with the same R's. K_{assoc} values with DMSO were found only for MeOH (K_{assoc} = 7.6 at 15 °C in CCl_4–DMSO mixture)[21a] and *t*-BuOH (K_{assoc} = 5.6 at 25 °C in C_2Cl_4–DMSO),[21b] and the ratio of the values (under slightly different conditions) is smaller than for **2a**/**2d**. The differences in K_{assoc} values with DMF in CCl_4 at 25 °C [4.4 ± 1.7 (H_2O),[10b] 5.5[21c] (4.2 at 28 °C)[21a] (MeOH), 3.5 (EtOH),[21c] and 2.9 (*t*-BuOH)[21c]] are smaller than in our system. From other data when Et_3N and pyridine are the bases,[22-25] the effect of alkyl group on K_{assoc} in aliphatic systems less crowded than **2** qualitatively resembles that for **2**.

However, the enolic OH group is more acidic than that of the simple aliphatic alcohols. The pK_a's of enols **2** should be somewhat higher than 9.40, the value for Ph_2C=CHOH,[26] lower than for trifluoroethanol (pK_a = 12.8)[27] and close to that of phenol (pK_a = 9.95).[28] Since K_{assoc} with $MeCONMe_2$ increases with the acidity of the alcohol,[29] our K_{assoc} values are expected to resemble those for TFE·DMSO (141)[29b] or PhOH·DMSO (202).[30] The

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[18] For earlier references, see: Shorter, J. In *Advances in Linear Free Energy Relationships*; Chapman, N. L., Shorter, J., Eds.; Plenum: London, 1972; Chapter 2. For recent references but opposite view, see: Hanson, P. *J. Chem. Soc., Perkin Trans. 2* **1984**, 101.

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[20] Abboud, J.-L. M.; Sraidi, K.; Guiheneuf, G.; Negro, A.; Kamlet, M. J.; Taft, R. W. *J. Org. Chem.* **1985**, *50*, 2870.

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[22] (a) Hirano, E.; Kozima, K. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1216. (b) Stevenson, D. P. *J. Am. Chem. Soc.* **1962**, *84*, 2849. (c) Singh, S.; Murthy, A. S. N.; Rao, C. N. R. *Trans. Faraday Soc.* **1966**, *62*, 1056. (d) Huiskens, P.; Huiskens, T. Z.; Dierckx, A. M. *Ann. Soc. Sci. Bruxelles* **1964**, *78*, 175.

[23] An estimate of the variability of the values from different laboratories is shown by K_{assoc} values for the MeOH–pyridine adduct: 3.0 and 2.9 (CCl_4, 25 °C, by IR),[25a] 2.3 (CCl_4, 25 °C, IR),[22b] and 6.0 (20 °C, near IR).[25b]

[24] (a) Findlay, T. J. V.; Kidman, A. D. *Aust. J. Chem.* **1965**, *18*, 521. (b) Rider, P. E.; Hammaker, R. M. *Spectrochim. Acta* **1973**, *29A*, 501.

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[28] Rappoport, Z. *Handbook of Tables for Organic Compounds Identification*, 3rd ed.; CRC: Cleveland, **1967**, p 434.

[29] Gramstad, T.; Sandström, J. *Spectrochim. Acta* **1969**, *25A*, 31. (b) Sherry, A. D.; Purcell, K. F. *J. Phys. Chem.* **1970**, *74*, 3535. (c) Guidry, R. M.; Drago, R. S. *J. Am. Chem. Soc.* **1973**, *95*, 759.

lower observed values probably result from stabilization of our enols by intramolecular hydrogen bond, whereas some of the values used for the comparison are for association of the free alcohol. Intramolecular competition for our enols will reduce appreciably the calculated K_{assoc} values.

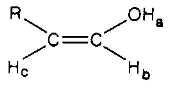
Nature of the Anti-Type Conformation. The solvent dependence of δ(OH), its correlation with β, the 1:1 association with DMSO, the shift in ν_{OH} of **2d** in DMSO compared with CCl_4, and analogy with the behavior of **1** point to the presence of a strongly hydrogen bonded conformation that differs from the one present in CCl_4. Structural information on the dihedral H–O–C=C angles in these two conformations in solution are not available. For **1** the two conformations were assigned as syn planar and anti clinal mainly on the basis of the correlation between H–C–O–H dihedral angles and the observed ^3J(HCOH) values.[31] The vicinity of the OH to the *cis*-mesityl group in CCl_4 (i.e. syn) and the much larger distance in DMSO (i.e., anti) was corroborated by the $\Delta\delta$(OH) values for isotopomeric 1,2-dimesityl-2-mesityl-*Me*-d_9-ethenols in various solvents.[2]

Circumstantial reasoning suggests that the two conformations are likewise for enols **2** syn-type and anti-type, respectively. First, the changes of the δ(OH) for **2** and **1** are qualitatively parallel. Second, the ν_{OH} of 3529 cm^{-1} in CCl_4 for **2d** suggests an internally hydrogen bonded conformation. Third, ab initio calculations on simpler systems[5] which indicate that only the syn planar and the anti planar conformations are minima on the potential energy surface suggest that the other conformer is anti.

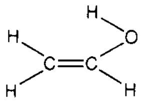
In analogy with the use of ^3J(HCOH) for **1**,[2] we hoped to obtain more definite conformational information from the relatively small ^4J(HCCOH) couplings and their solvent-dependence. Many analogous ^4J(HCCCH) values were measured, tabulated,[32,33] and found to be sensitive to the conformation, and it is usually accepted and supported by ab initio calculations[34] that the maximum coupling is for a W-shape arrangement of the H–C–C–C–H system.[32]

However, a Karplus-type relationship between the ^4J values and the two dihedral angles in the HCCCH moiety is not available and it is not known if the above generalization applies for the HOCCH moiety. Only limited data are available for a saturated HOCCH skeleton[35] and more data for phenols.[35a] Both $^3J(H_bCOH_a)$ and $^4J(H_cCCOH_a)$ were measured for vinyl alcohol **3a**[4c] and for (*Z*)-1-propenol (**3b**)[4a,b] in acetone containing 0.72–1.48% H_2O. The ^3J values indicate major contributions from the syn conformer (**4a**) for **3a** and of the anti conformer (**4b**) for **3b**. The higher ^4J for **4a** suggested that the W relationship holds also for the HCCOH moiety.

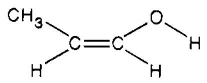
^4J(HCCOH) values were measured for the geminal $H_3CC(OH)$ moiety in diastereomeric PhC(OH)(Me)CHRCOOR′.[36] Analysis of the data suggested that in $CDCl_3$ and $C_6D_5CD_3$ $^4J_{HOCCH_3}$ = 0.92–1.10 Hz for a conformer with favored W conformation and zero for a conformer that cannot achieve that conformation. In DMSO-d_6 ^4J = 0 for both diastereomers. Tables I and II show a more complicated situation in our system. Rather than the expected gradation in ^4J on increasing β, ^4J(HOCCH) for **2c** is 1.6 Hz in all our solvents except for DMSO and DMF where it is 0. Likewise, ^4J changes slightly from 1.57 to 1.34 Hz from CCl_4 up to 6.6% DMSO in CCl_4 whereas the parallel change in δ(OH) is appreciable (Tables I and III), and at higher percentages of DMSO ^4J = 0. Moreover, for **2a** ^4J decreases by 0.32 Hz from $CDCl_3$ to $C_6D_5CD_3$, although by analogy with **1**, less syn conformer should be present in $CDCl_3$.



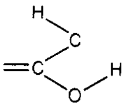
3a: R = H J_{ab} = 9.8 Hz, J_{ac} = 0.4 Hz
b: R = Me J_{ab} = 6.0 Hz, J_{ac} = 0.8 Hz



4a



4b



5

The ^4J value in CCl_4 is consistent with a syn (W) arrangement. From the small change in ^4J where δ(OH) values change appreciably this conformer is now in equilibrium with another conformer having a close ^4J value. The observation that a "sickle" anti-type conformation **5** can have an appreciable ^4J[37] can explain the behavior in all solvents except DMSO and DMF, but further discussion is unwarranted until more data on the dependence of ^4J on the HCCOH conformation[38] become available.

δ(OH) Correlations. A monotonic relationship between $\delta_{anti\cdot DMSO}$ and δ_{DMSO} values is not unexpected since both $\delta_{anti\cdot DMSO}$ and $F_{anti\cdot DMSO}$ in pure DMSO are higher for the more associated enols. If the linearity between the two δ sets (eq 12) is more general, then the available δ_{obsd} values rather than the more appropriate but usually unavailable δ(OH) of the hydrogen bonded conformation could be correlated with solvent parameters. An example is the approximate linear correlation between δ(OH) for **2** and Kamlet–Taft's β[3] in eight solvents (Figure 2), which indicate that for enols **2** the interaction responsible for the shift in δ(OH), and presumably for a conformational change, is hydrogen bonding with the solvent. The multiparameter full solvatochromic correlation[3] was not applied for **2** since for enol **1** β is the only parameter of significance in this equation and δ(OH) for **2** are linearly correlated with δ(OH) for **1** (Figure 1). Figure S2 is of interest since the linearity between log K_{assoc} and C is another probe which suggests that hydrogen bonding to the solvent becomes weaker when R is changed from H to *t*-Bu.

The correlation between log K_{assoc} and $\delta_{anti\cdot DMSO}$ (Figure 5) is a manifestation that "the difference in chemical shifts for unassociated and associated HA can be used as an indication of hydrogen bond strength".[11c] Correlations between log K_{assoc} and the limiting $\delta(^{19}F)$ of the adducts of *p*-fluorophenol or 5-fluoroindole with many bases were previously observed.[39] In our system the change is in the

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(38) Many calculations for ^4J's at various combinations of the dihedral angles are given in ref 32d. In view of the dependence of the values on the method used, they are of little help in respect to our problem.

(39) (a) Gurka, D.; Taft, R. W. *J. Am. Chem. Soc.* **1969**, *91*, 4794. (b) Mitsky, J.; Joris, L.; Taft, R. W. *Ibid.* **1972**, *94*, 3442.

structure of the enol rather than in that of the base. This is reasonable since the stronger the association (K_{assoc}), the more deshielded the hydroxylic proton.

The sensitivity of log K_{assoc} to δ(OH) is high. The slope of eq 14 is 0.77. A 2.7-fold change in K_{assoc} (**2a** → **2d**) results in a shift of δ(OH) by 0.71 ppm. In a single family the δ(OH) can thus serve as a sensitive tool for the degree of association. However, δ(OH) in our system is affected not only by hydrogen bonding but also by the ring currents, i.e., by the location of the OH relative to the faces of the β-mesityl rings. The regular changes in both the MesC=C dihedral angles and the R–C–O bond angle from R = H to R = *t*-Bu may contribute to the regular change of δ(OH) on changing R.

Conclusions

The α-alkyl-β,β-dimesitylethenols **2** exist in CCl_4 in a syn-type conformation and in DMSO in an anti-type conformation associated with a solvent molecule. The association constant with DMSO (K_{assoc}) decreases with α-R in the order H > Me > Et > *i*-Pr > *t*-Bu. The log K_{assoc} values are linear with σ^* of the α-substituent, indicating a major contribution from a polar effect. They decrease nonlinearly with the steric parameter E_s, probably reflecting that the association occurs at a relatively unhindered side of the molecule.

Experimental Section

Enols **1** and **2a–d** were prepared as described previously.[2,6] CCl_4 was dried over 4A molecular sieves, and the deuteriated NMR solvents were the best commercial samples. NMR spectra were recorded with a Bruker WP 200 SY pulsed FT spectrometer operating at 200.133 MHz. IR spectra were recorded with a Analect FTIR FX-6200 spectrometer.

Acknowledgment. This work was supported by a grant from the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel, to which we are grateful.

Registry No. 1, 54288-04-9; **2a**, 89959-15-9; **2b**, 96040-90-3; **2c**, 96040-91-4; **2d**, 89959-16-0.

Supplementary Material Available: Figure S1 showing the linearity of the plot according to eq 9 and Figure S2 showing a linear K_{assoc} vs C plots (3 pages). Ordering information is given on any current masthead page.

Conformational Effects in the Alkali-Metal Reduction of Diaryl Sulfides. 2. Evidence for Episulfide Intermediates

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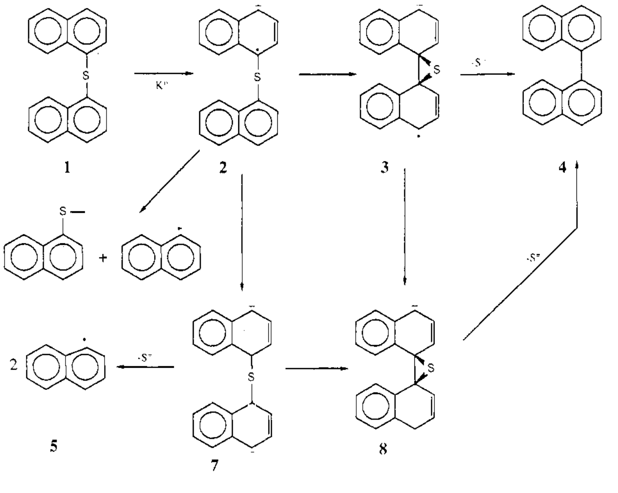
Received January 28, 1988

Alkali-metal reduction of a series of diaryl sulfides shows that, if both aryl moieties possess aromatic stabilization energies less than that of the phenyl group (i.e., able to generate relatively more stable radical anions), the diaryl sulfide forms an episulfide intermediate via regiospecific coupling of the aryl moieties at the stage of a reactive intermediate. The formation of the episulfide intermediate explains why double carbon–sulfur bond cleavage and extrusion of sulfur is observed only in such diaryl sulfides and why there is a preference for the formation of single regioisomeric biaryl.

Introduction

In our previous work on the alkali-metal reduction of diaryl sulfides,[1] we have shown that the conformational freedom available to the aryl groups allows maximum orbital overlap at the stage of a reactive intermediate, probably that of the radical anion (Scheme I). This overlap in turn leads to facile cleavage of the carbon–sulfur bond.[2] Molecules similar in structure to diaryl sulfides but lacking this conformational freedom, such as dibenzothiophene, cannot achieve such maximum orbital overlap during reduction. For this reason ring hydrogenation of dibenzothiophene occurs without cleavage of the carbon–sulfur bond. In diaryl sulfides that are capable of generating relatively stable radical anions (those with aryl moieties more extensively conjugated than phenyl, such as naphthyl or quinolyl), there was some evidence[1] of coupling of the aryl moieites at some reactive intermediate stage to form an episulfide which extrudes sulfur with two carbon–sulfur bond cleavages to give the corresponding biaryl. The coupling was specifically shown (Scheme I) to occur before carbon–sulfur bond cleavage. The reaction, as shown, is essentially an aryl migration. Intramolecular attack of reactive intermediates such as radicals and anions

Scheme I



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0022-3263/88/1953-4821$01.50/0 © 1988 American Chemical Society