Table II. $^{13}C-^{1}H$ and $^{13}C-^{13}C$ Coupling Constants (Hz) in **1**

$^1J(^{13}C-^1H)$		$^1J(^{13}C-^{13}C)$	
$C_{14}-H_{14}$	153.0	$C_{14}-C_{15}$	48.8
$C_{15}-H_{15}$	173.3	$C_{14}-C_{13}$	61.8
$^2J(^{13}C-^1H)$		$^3J(^{13}C-^{13}C)$	
$C_{14}-H_{15}$	10.6	$C_{14}-C_{12a}$	4.5
$C_{15}-H_{14}$	<1.5	$C_{14}-C_{11}$	6.0
		$C_{15}-C_{12a}$	broadening
$^3J(^{13}C-^1H)$		$C_{15}-C_{12}$	5.1
$C_{14}-C_{13}H_3$	7.5	$C_{15}-C_{13}H_3$	broadening

enrichment is found at the expected chemical shift value, at 122.0 and 159.3, respectively. In the spectrum of the $^{13}C_2$-enriched compound **1c**, at 122.0 and 159.3 an AB pattern [$^1J(^{13}C-^{13}C) = 48.8$ Hz] is observed, together with the singlets due to the 2× 10% monolabeled material, which is in agreement with the enrichment determined by mass spectrometry. The spectra clearly demonstrate that no scrambling has occurred. The ^{13}C-enriched compounds also contain the natural abundance amount (1.1%) of ^{13}C at each of the nonenriched positions. This implies that in the singly labeled compounds ^{13}C pairs involving the enriched position are present at a level of approximately 1% (0.9 × 1.1%). From the ^1H noise-decoupled 100-MHz ^{13}C NMR spectra at the natural abundance level, the $^{13}C-^{13}C$ coupling constants are obtained. The values are summarized in Table II. In the proton noise-decoupled 50-MHz ^{13}C NMR spectra of the deuteriated seven-membered rings **1d**, **1e**, and **1f**, the deuterium-carrying carbon atom has a low intensity or is lost in the noise owing to the low magnetic moment and the absence of the NOE.[39]

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[39] Breitmeier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*, 3rd ed.; VCH Gesellschaft: Weinheim, 1987.

Direct Observation of Intramolecular Hydrogen Bonding of a Hydroxy Proton to an Indenide Carbanion in Apolar and Polar Non-Hydrogen Bond Donor Solvents by NMR and IR Spectroscopy

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Abstract: To obtain information about the elusive hydrogen-bonded carbanions, which are postulated as intermediates in proton-transfer reactions from carbon acids, the molecule 4-(3′-indenyl)-2,3,4-trimethyl-2-pentanol (**1**) has been designed and synthesized. The carbanion **2** generated in polar non-hydrogen bond donor solvents from the precursor **1** showed the presence of long-lived intramolecular hydrogen bonding of the hydroxy group to the carbanionic part (cf. **2a**). It was discovered that in the presence of cryptand C211 carbanion **2** rather than the oxyanion **3** was formed in apolar non-hydrogen bond donor solvents upon reaction of **1** with butyllithium. An extensive study of this interaction in solvents like dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), pyridine, benzene, and toluene using NMR and IR spectroscopy has been carried out. For example, in benzene the OH proton in **2** appeared in the ^1H NMR spectrum 3.2 ppm downfield of the corresponding proton in the precursor **1**. In the IR spectrum, the OH stretching band of **2** appeared shifted 274 cm^{-1} to lower frequency relative to that of **1**. Also consistent with the structure **2a** for carbanion **2** was the observed small temperature dependence of the ^1H NMR chemical shift of the OH proton which is typical for intramolecular hydrogen bonding. Nuclear Overhauser enhancement (NOE) studies also strongly support the proposed structure **2a** for the carbanion.

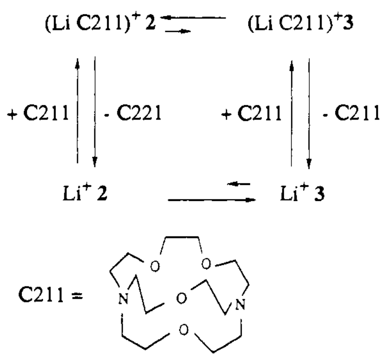
Introduction

Knowledge about the elusive hydrogen-bonded carbanions, which are postulated as intermediates in proton-transfer reactions, is meager, as is the knowledge of the specific solvation of carbanions in general. There are only a few reports on hydrogen bonding by bulk solvent to carbanions[1] and hydrogen bonding to an isonitrile.[2] In the solid state, crystallographic studies have shown the presence of hydrogen bonding to carbanions,[3] and in the gas phase the strength of hydrogen bonds to acetylides has been measured using ion cyclotron spectroscopy.[4]

Our work in this area has been focused on designing reaction systems with the potential to yield hydrogen-bonded carbanions with lives long enough to allow direct observation of such species by NMR, IR, and UV spectroscopy.[5]

In our attempts to develop systems with hydrogen bonding of OH to the carbanions, we initially used DMSO[6] as solvent and

Scheme I



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[1] (a) Ford, W. T. *J. Am. Chem. Soc.* **1970**, *92*, 2857. (b) Hogen-Esch, T. E. *J. Am. Chem. Soc.* **1973**, *95*, 639. (c) Greifenstein, L. G.; Pagani, G. A. *J. Org. Chem.* **1981**, *46*, 3336. (d) Mueller-Westerhoff, U. T.; Nazzal, A.; Proessdorf, W. *J. Am. Chem. Soc.* **1981**, *103*, 7678.

[2] (a) Ferstandig, L. L. *J. Am. Chem. Soc.* **1962**, *84*, 1323. (b) Ferstandig, L. L. *J. Am. Chem. Soc.* **1962**, *84*, 3553. (c) Schleyer, P. v. R.; Allerhand, A. *J. Am. Chem. Soc.* **1962**, *84*, 1322. (d) Allerhand, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1963**, *85*, 866.

[3] (a) Seebach, D. *Angew. Chem.*, Int. Ed. Engl. **1988**, *27*, 1624. (b) Buchholz, S.; Harms, K.; Massa, W.; Boche, G. *Angew. Chem.* **1989**, *101*, 73.

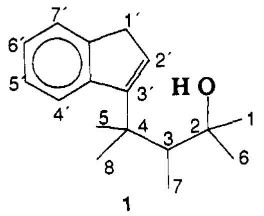
[4] Caldwell, G.; Rozeboom, M. D.; Kiplinger, J. P.; Bartmess, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 4660.

[5] (a) Ahlberg, P.; Johnsson, B.; Mc Ewen, I.; Rönnqvist, M. *J. Chem. Soc., Chem. Commun.* **1986**, 1500. (b) Ahlberg, P.; Davidsson, Ö. *J. Chem. Soc., Chem. Commun.* **1987**, 623. (c) Ahlberg, P.; Davidsson, Ö; Johnsson, B.; Mc Ewen, I.; Rönnqvist, M. *Bull. Soc. Chim. Fr.* **1988**, *2*, 177. (d) Mc Ewen, I.; Ahlberg, P. *J. Chem. Soc., Chem. Commun.* **1989**, 1198.

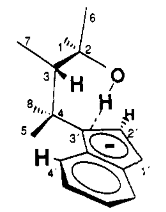
0002-7863/92/1514-10869$03.00/0

thus took advantage of the extensive knowledge of pK_a values of carbon acids and oxygen acids in this solvent.[7] Indenes and fluorenes are about 10^6–10^9 times stronger acids than alcohols in DMSO.

In the present work, which was recently communicated, the compound 4-(3′-indenyl)-2,3,4-trimethyl-2-pentanol (**1**) was designed to yield the intramolecularly hydroxy group hydrogen bonded carbanion **2a** upon carbanion formation. The length of the side chain of the indenide (i.e., the pentanol main chain) was chosen so that a six-membered chelate ring with a C$^-$···H–O hydrogen bond could be formed. The five methyl substituents on the side chain were introduced for the purpose of directing the OH group toward the carbanion. Extensive studies using NMR and IR spectroscopy of the carbanion generated from **1** in a number of apolar solvents, in the presence of cryptand C211,[6] and in polar non-hydrogen bond donor solvents (Scheme I) strongly suggest that it has the structure **2a**.



1

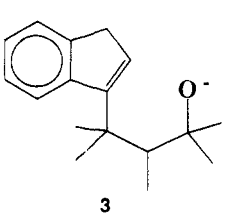


2a

Results and Discussion

To begin with, results of studies of the solvent and counterion dependence of the oxygen acid vs carbon acid acidity of compound **1** will be presented. Then, IR spectroscopic investigations will be discussed, followed by results of ^{1}H NMR spectroscopic studies of the hydroxy protons and conformational studies.

Solvent Dependence of Oxygen Acid vs Carbon Acid Acidities. At the outset of this project, DMSO was used as solvent since the carbon acid of **1** was predicted to be a stronger acid than its oxygen acid in this solvent. Indeed, an intensively yellow colored solution was obtained upon treatment of racemic **1** with butyllithium (BuLi) or dimsylpotassium in DMSO, indicating the formation of **2**. Similar results were also obtained in other polar non-hydrogen bond donor solvents like DMF[6] and DMPU,[6] as indicated by ^{1}H NMR spectroscopy. The carbanion **2** was also generated in mixtures of these solvents with acetonitrile, pyridine, THF,[6] benzene, and diethyl ether. The solutions contained up to 60–90% of the latter component. However, with pure THF a colorless solution was obtained upon reaction of **1** with BuLi, i.e., the alkoxide ion **3** rather than the indenide **2** was formed. In pyridine, on the other hand, a mixture of oxyanion and carbanion (<10 mol %) was obtained.



3

Interestingly, the addition of cryptand C211[6] to a solution of the lithium alkoxide ion **3** in THF turned the solution yellow. The presence of both an indenide ion and an alcohol group was confirmed by ^{1}H NMR spectroscopy. No alkoxide was detected.

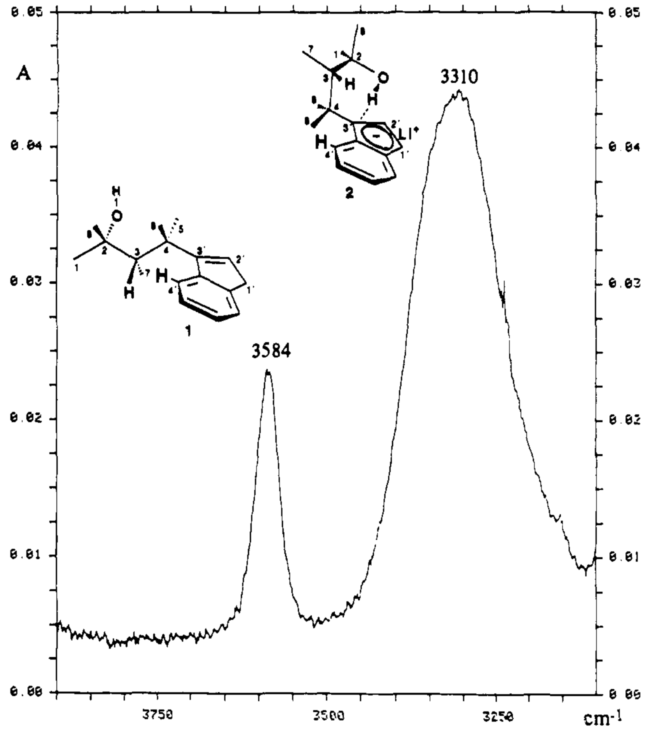


Figure 1. FT-IR absorption spectrum for a mixture of **1** (8.7 mM) and **2** (7.7 mM) with cryptand C211 (10 mM) in benzene at 21 °C.

Evidently, the addition of cryptand C211 lowered the apparent acidity of the O–H bond in **2** by removing the strong bonding between the Li$^+$ and oxide ions. In pure THF, both the carbanion **2** and the alkoxide ion **3** are assumed to be paired with lithium cations. The Li$^+$–**3** pair is possibly more stable than the Li$^+$–**2** pair because the Li$^+$–alkoxide interaction is stronger than the Li$^+$–indenide one. Addition of the cryptand C211, which has been designed to complex lithium cations particularly well, separates the lithium cations from **3** and **2**. As a result, the stronger basicity of **3** is expressed and, thus, the carbanion **2** is favored in the equilibrium (cf. Scheme I). Related ion-pairing effects have been reported previously.[8] This finding has been most useful in our investigations of hydrogen-bonded carbanions. Thus, employing the cryptand has made it possible to prepare the carbanion **2** not only in THF but also in other apolar solvents like pyridine, benzene, and toluene.

IR Spectroscopic Studies. In DMSO, the OH proton in the precursor **1** is strongly hydrogen bonded to the solvent, as manifested by an OH stretching band at 3393 cm^{-1} in the IR spectrum.[9] Upon formation of carbanion **2** from **1**, the frequency of the stretching band from the OH group changed to 3316 cm^{-1}, i.e., shifted 77 cm^{-1} to lower frequency. Furthermore, the band became broader and more intense than that of **1**. In mixtures of **1** and **2**, the bands overlap and, therefore, only one broad band is observed.

In mixtures of DMSO with other solvents like benzene, diethyl ether, and pyridine, the OH groups in **1** and **2** showed stretching bands at about the same frequencies as in pure DMSO; i.e., the bands were some 80 cm^{-1} apart, and the band from **2** was broader and more intense.

In pure benzene, the OH stretching band of **1** appears at 3584 cm^{-1}, indicating that the OH proton is only weakly hydrogen bonded to the solvent. The IR spectrum of an equimolar mixture

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(6) Abbreviations used in this paper: DMSO = dimethyl sulfoxide; DMF = dimethylformamide; DMPU = 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (*N,N′*-dimethyl-*N,N′*-propyleneurea); THF = tetrahydrofuran; C211 = 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane (cf. Scheme I).

(7) (a) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Margolin, Z.; Mc Collum, R. J.; Mc Collum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006. (b) Olmstead, W. N.; Margolin, Z.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 3295. (c) Bordwell, F. G.; Drucker, G. E. *J. Org. Chem.* **1980**, *45*, 3325.

(8) (a) Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1966**, *88*, 307. (b) Hogen-Esch, T. E. In *Advances in Physical Organic Chemistry*; Gold, V., Bethell, D., Eds.; Academic Press: New York, 1977; Vol. 15. (c) Smid, J. In *Ions and Ion-pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley: New York, 1972. Gronert, S.; Streitweiser, A. *J. Am. Chem. Soc.* **1988**, *110*, 2836 and references therein.

(9) Joesten, M. D.; Schaad, L. J. *Hydrogen bonding*; Marcel Dekker, Inc.: New York, 1974; p 42.

Table I. ^1H NMR Chemical Shifts of the OH Protons and IR Stretching Frequencies of the OH Bonds in **1** and **2** in DMSO, Pyridine,[a] THF,[a] Benzene,[a] and Toluene[a]

	^1H chemical shift[b]		stretching band[c]	
solvent	**1**-OH, ppm	**2**-OH, ppm	**1**-OH, cm^{-1}	**2**-OH, cm^{-1}
DMSO	4.02	3.61	3393	3316
pyridine	5.26	4.78		
THF	3.16	3.89	3469	3324
benzene	1.29	4.53	3584	3310
toluene	1.39	4.54		

[a] An equimolar amount of C211 to **2** was added to the solution. [b] The reference chemical shifts for remaining carbon-bonded protons: in DMSO-d_6, 2.50 ppm; in pyridine-d_5, 8.70 ppm; in THF-d_8, 3.58 ppm; in benzene-d_6, 7.20 ppm; and in toluene-d_8, 2.30 ppm. The chemical shift of the OH proton in **1** in pyridine, THF, benzene, and toluene was independent of the presence of cryptand or carbanion. ^1H NMR spectra were obtained in DMSO at 30 °C and in the other solvents at 21 °C. The concentration of the solute was ca. 15 mM. [c] The IR and ^1H NMR spectra were obtained at 21 °C at similar concentrations.

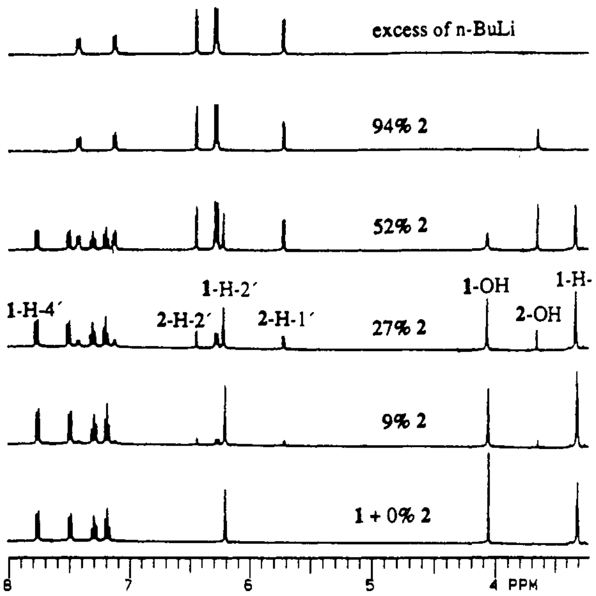


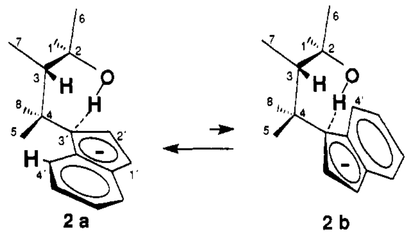
Figure 2. ^1H NMR spectra at 30 °C of **1** and mixtures of **1** and **2** in DMSO. The mixtures were obtained by titration of a 0.16 M solution of **1** with *n*-BuLi.

of **1** and **2** in the presence of C211 showed two well-separated OH stretching bands (Figure 1). The band originating from the carbanion **2** appeared at 3310 cm^{-1}, i.e., shifted 274 cm^{-1} to lower frequency relative to the band from **1**. Again, the band from **2** was much broader and more intense than that from **1**. In THF, the OH stretching band of **1** was observed at 3469 cm^{-1} and that of **2** at 3324 cm^{-1}. Therefore the bands are only partially resolved in mixtures of **1** and **2** in THF.

The results obtained with the different solvents are summarized in Table I. The stretching frequency of the OH group in **2** appears to be essentially independent of the solvent, in contrast to the band from **1** that shows strong dependence. The conclusion is that upon formation of **2** the OH proton prefers to be intramolecularly hydrogen-bonded; i.e., carbanion **2** has the structure **2a**. In this structure the OH proton is essentially unperturbed by the solvent, as indicated by the solvent independence of the OH stretching frequency. On the other hand, the solvent dependence of the stretching frequency of **1** shows the pattern expected from intermolecular hydrogen bonding to the solvent.[10]

NMR Studies of Compounds 1 and 2. Figure 2 shows ^1H NMR spectra of **1** and mixtures of **1** and **2** in DMSO. The mixtures have been obtained by titration of a 0.16 M solution of **1** with *n*-BuLi. The OH proton resonance of **1** appears at 4.02 ppm. In mixtures of **1** and **2** the OH peak from **2** appears at 3.61 ppm, and the peak from **1** remains at 4.02 ppm. At first glance this was a surprising result, considering the IR results presented above. Stronger hydrogen bonding usually results in deshielding rather than shielding of the hydrogen-bonded proton. However, the structure of **2a** suggests that the OH proton also should experience a shielding effect due to ring currents in the carbanionic aromatic five-membered ring.

Scheme II



It is interesting to note that the chemical shifts of the carbon-bonded protons of the carbanion part of **2** closely resemble those of other 1-substituted indenides. This may indicate that the intramolecular hydrogen bond leaves the indenide of **2** essentially unperturbed.

It should also be mentioned that the OH proton chemical shifts of **1** and **2** are independent of the counterion. No significant shift change is measured upon exchanging Li^+ for K^+. Upon addition of about 1 equiv of base (*n*-BuLi or CH_3SOCH_2K), the OH peak of **2** disappeared due to fast proton exchange with DMSO.

The addition of other non-hydrogen bond donor solvents to a mixture of **1** and **2** in DMSO caused chemical shift changes of both types of OH protons. Experiments indicated the presence of small amounts of alkoxide ions. The OH proton chemical shifts of **1** and **2** in various solvents are summarized in Table I.

The addition of small amounts of water to any of the carbanion solutions did not affect the shape or chemical shift of the OH proton signal; i.e., the intramolecular hydrogen bonding of the carbanion was unperturbed. In contrast, the hydroxy proton in **1** rapidly broadened due to exchange with H_2O protons. Cryptand C211 had to be added to all solutions to avoid the precipitation of LiOH and the accompanying quenching of the carbanion.

Conformational Studies by ^1H NMR. Additional support for structure **2a** has been obtained through the use of ^1H nuclear Overhauser enhancements (NOE) associated with **2** (cf. Experimental Section). The tool used was two-dimensional NOE spectroscopy (NOESY). Such spectroscopy is commonly used to study NOE effects in macromolecules for structure determination, but it has so far found only little use in the study of the structure of small molecules.[11]

NOESY spectra were obtained from mixtures of **1** and **2** in DMSO, DMF, THF, and benzene. The results support the structure **2a** but also show the presence of a small fraction of another conformer, which possibly is **2b** (Scheme II). This was deduced from the presence of a small cross peak of H-8 and H-4′ and observations at low temperature by 1D NMR. Semiempirical calculations indicate a small energy difference between **2a** and **2b** in favor of **2a**.[12] However, it should be mentioned that attempts to observe a NOE on the 3′-carbon in **2a** due to the proximity of the OH group in this structure were unsuccessful. Low-temperature studies revealed the presence of more than one conformer of **1**.

The temperature dependence of the chemical shifts of the OH protons of compounds **1** and **2** has also been studied. The temperature dependence of the OH chemical shift in **1** was large in DMSO, DMF, and THF/DMPU, as expected from intermolecular hydrogen bonding. In contrast, the chemical shift of the OH group of **2** showed only a small temperature dependence, consistent with intramolecularly hydrogen bonded structure **2a**.[13]

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(10) Joesten, M. D.; Schaad, L. J. Reference 9, pp 3–7.

(11) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy, A guide for Chemists*; Oxford University Press: Oxford, 1987; pp 171, 227.

(12) Mc Ewen, I. *J. Mol. Struct.: THEOCHEM*, in press.

Thus all evidence presented above clearly indicates that the studied carbanion **2** mainly consists of one conformer, the designed one, represented by the conformation **2a**.

Experimental Section

Materials. All starting materials were obtained from commercial suppliers, and the deuterated solvents were dried over molecular sieves (4 Å). THF-d_8 was stored over Deperox (Fluka AG) and distilled in an N_2 atmosphere prior to use. DMSO (nondeuterated) was distilled from $NaNH_2$. The carbanion precursor **1** was synthesized from 3,4-dimethyl-3-penten-2-one and indene as previously reported.[5b]

General Procedures. All preparations and manipulations were made in an N_2 atmosphere in a stainless steel Mecaplex GB80 glovebox equipped with a gas purification system. The water content (1–2 ppm) in the atmosphere was measured with a Shaw hygrometer (Model SHA-TR). Glassware and syringes were dried in a vacuum oven (3 Pa) at 50 °C overnight before introduction of the equipment into the glovebox.

The solutions of the carbanion **2** and the precursor **1** were prepared by adding a solution of 2.5 M *n*-BuLi in *n*-hexane (the amount depended on the desired [**2**]/[**1**] ratio) with a syringe to a screw-capped 5-mm NMR tube equipped with a septum and containing a preweighed amount of the precursor **1** in 0.6 mL of the solvent.

This method was employed for dilute solutions (<30 mM). Thus the amount of hexane introduced was small and could be decreased even more by using 10 M *n*-BuLi. Hexane-free solutions were prepared in the following way. First, the hexane was removed from the *n*-BuLi on a vacuum line, and then a solution of **1** was introduced with a gastight syringe under a flow of nitrogen either at room temperature or while cooling the vessel in liquid nitrogen.

Since some solvents, e.g., DMF and pyridine, react with *n*-BuLi, the following procedure was used with such solvents. First, alkoxide **3** was made from **1** by reaction with *n*-BuLi in THF, and then the THF was evaporated before the desired solvent was added. The addition of cryptand was made either before or after the addition of *n*-BuLi to a solution of **1** in THF, pyridine, benzene, or toluene.

IR Spectroscopy. Spectra were obtained with a Perkin-Elmer 1800 FT-IR at 21 °C. The windows of the cell were made of CaF_2 and separated by a 0.3-mm Teflon spacer. The number of transients was between 10 and 60, depending on the concentration of the carbanion solution. A carbanion spectrum was obtained by subtracting the spectrum of the solvent. In this way overtones from the solvent in the region between 3000 and 3700 cm^{-1} were eliminated.

NMR Spectroscopy. The data were acquired and processed with a Varian XL 400 spectrometer operating at a ^1H frequency of 399.917 MHz and a ^{13}C frequency of 100.571 MHz. A 5-mm broad band dual probe was used for the investigations. The number of transients for the proton spectra was ca. 100, and a 16K transform was carried out over a spectral width of about 4500 Hz. The pulse angles used were between 30° and 60°. However, when large proportions of nondeuterated solvents were used, either the pulse angle was shortened to less than 3° or a 10-dB attenuator was introduced between the observe amplifier and the observe receiver.

The length of the 90° pulse was checked before the T_1 and 2D experiments. The 90° ^1H pulse lasted for 32 μs, and the corresponding ^{13}C pulse lasted for 14 μs. In all 2D experiments, two dummy transients were dumped before acquisition of each new incremental spectrum.

The homonuclear ^1H shift correlated (COSY) 2D NMR spectrum of **1** in DMSO-d_6 at 30 °C was obtained using phase cycling and the standard acquisition sequence with a 90° mixing pulse. A delay of 0.3 s was applied before and after the mixing pulse to emphasize long-range couplings. The spectral width was 3200 Hz, and the relaxation delay between the pulses was 4.5 s. Four 0.5K transients were acquired for each of the 100 incremental spectra. An experiment lasted for about 1 h.

The ^{13}C–^1H shift correlated (HETCOR) 2D spectrum of a mixture of **1** and **2** in DMF-d_7 at 21 °C was obtained with a fully decoupled standard acquisition sequence. The ^1H spectral width was 3200 Hz, and the one for ^{13}C was 15 800 Hz. The relaxation delay was 4 s, and 16 1K transients were acquired for each of the 128 incremental spectra. The experiment lasted for 2.5 h. The FID and the interferogram of both the COSY and the HETCOR were processed with a Gaussian apodization function.

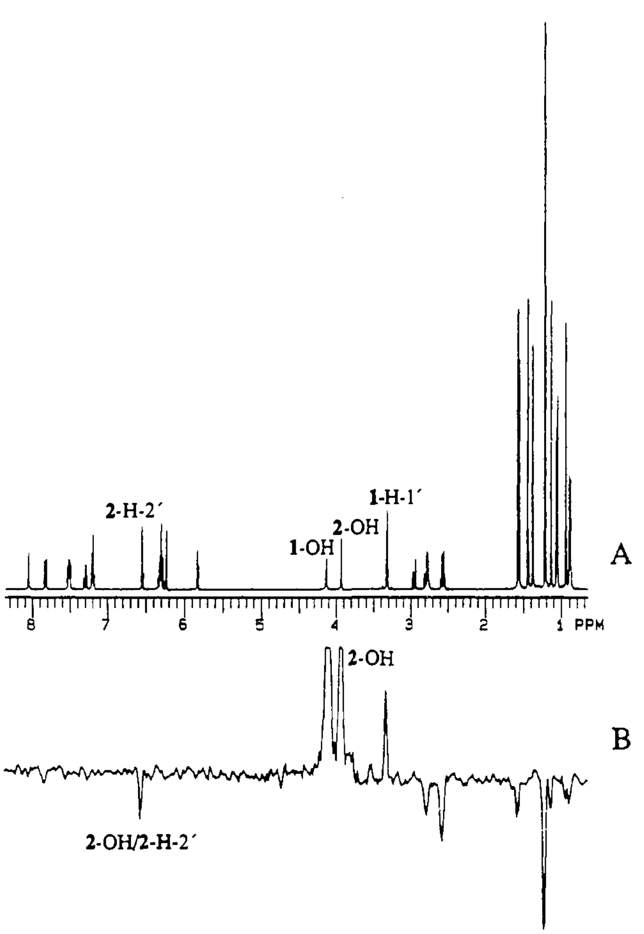

Figure 3. (A) ^1H NMR spectrum of **1** (0.08 M) and **2** (0.08 M) in DMF-d_7 at 21 °C. (B) Trace or skyline projection of the spectrum at 3.95 ppm along the f_2 axis corresponding to the OH proton in **2**, extracted from a phase-sensitive NOESY spectrum of the above mixture at the same temperature. The T_1 relaxation time of the OH protons was 2.9 s, and the mixing time used was 3 s. The positive peaks are due to magnetization transfer by chemical exchange, and the negative peaks are due to NOEs.

Table II. Carbon[a] and Proton Chemical Shifts[a] and Coupling Constants (J_{HH}) for **1** and **2** in DMSO-d_6

	1			**2**		
carbon no.[b]	δ ^{13}C, ppm	δ ^1H,[a] ppm	J_{HH}, Hz	δ ^{13}C, ppm	δ ^1H, ppm	J_{HH}, Hz
1	28.73	1.12[c]		25.57	1.06[c]	
2	73.32			74.17		
3	36.55	2.41, q	7.2	38.93	2.59, q	7.2
4	40.41			38.05		
5	25.80	1.30[c]		32.83	1.37[c]	
6	30.62	1.12[c]		33.11	0.90[c]	
7	12.98	0.80, d	7.2	13.58	0.98, d	7.2
8	26.33	1.48[c]		24.84	1.48[c]	
1′	46.38	3.26, dt	2.0, 23.8[d]	91.81	5.67, d	3.5
2′	126.16	6.17, t	2.0	116.36	6.39, d	3.5
4′	122.35	7.72, d	7.6	118.75	7.37, m	2.3
5′	125.41	7.25, t	7.1	110.17	6.23, m	2.3
6′	123.71	7.15, t	7.1	110.17	6.23, m	2.3
7′	123.89	7.55, d	7.5	118.03	7.08, m	2.3
OH proton		4.02			3.61	

[a] The reference chemical shifts for remaining carbon-bonded protons in DMSO-d_6 were set at 2.50 ppm and 39.50 ppm for carbon. [b] C-3′, C-3′a, and C-7′a could not be assigned with certainty. Corresponding peaks for **1** appeared at 154.68, 145.23, and 143.67 ppm and for **2** at 131.05, 125.00, and 112.30 ppm. [c] The methyl groups CH_3-1 and CH_3-6 are diastereotopic, as are CH_3-5 and CH_3-8. [d] ABX spectrum.

The NOESY experiments were performed in the phase-sensitive mode. The spectral width used was 4500 Hz, and 16 1K transients were acquired for each of the 256 or more incremental spectra. The mixing time was set equal to the T_1 relaxation time of the OH proton and was 1–3 s. Other mixing times different from the T_1 relaxation time of the OH proton were also used to test the response of the signals. The relaxation

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(13) (a) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman and Company; New York, 1960; p 146. (b) Merrill, J. R. *J. Phys. Chem.* **1961**, *65*, 2023.

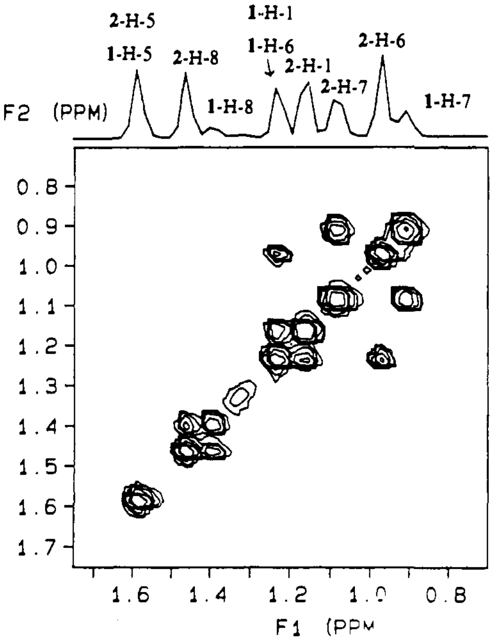

Figure 4. Expanded contour plot of a phase-sensitive NOESY spectrum of **1** (0.13 M) and **2** (0.23 M) in DMF-d_7 at 21 °C. Only positive contours due to magnetization transfer by chemical exchange have been plotted; the negative contours due to NOEs have been omitted.

delay was set equal to $2T_1$, and the T_1 relaxation time became shorter the higher the concentration of the carbanion.

The FID and the interferogram were processed with a very mild line-broadening function (0.1 Hz) and an apodization function equal to 0.6 × AT (AT = acqusition time; the acquisition time of the interferogram is equal to the number of increments divided by the sweep width). The NOESY experiments in DMSO were carried out at 30 °C. In experiments employing partially deuterated solvents, selective homodecoupling of the solvent signal was applied. With DMF-d_7 the NOESY experiments were carried out at 21 °C (cf. Figure 3) and at −60 °C.

The sample temperature in the probe was measured using a calibrated thermocouple of type K introduced into a 5-mm NMR tube. The resistance temperature detector Pt 100 DIN 1/10 was used as a reference.

Assignments

The assignment of ^{1}H and ^{13}C NMR signals was carried out mainly by well-known means, including COSY, NOESY, and selective decoupling. Also, exchange of protium for deuterium was employed. The assignment of the methyl peaks in the ^{1}H NMR spectra of **1** and **2** was more difficult, since out of the five methyl groups only one appears as a singlet. The methyl groups CH_3-1 and CH_3-6 on the carbon bonded to the hydroxy group are diastereotopic, as are the CH_3-5 and CH_3-8 methyl groups. The assignment of the methyl peaks was made by employing deuterium isotope effects on the ^{13}C chemical shifts caused by exchange of ^{1}H for ^{2}H in the hydroxy group of **1**. The spectrum of partially deuterated **1** showed that carbons in deuterated **1** had shifted upfield. Using the knowledge that the shift becomes smaller the further away the carbon is from the alcohol group,[14] C-2 was assigned to the carbon that shifted 0.11 ppm upfield. Carbons C-1, C-3, and C-6 all showed smaller upfield shifts, ~0.06 ppm. A ^{13}C–^{1}H shift correlated (HETCOR) 2D spectrum of **1** in DMSO was obtained, and the methyl peaks were assigned using the knowledge about the ^{13}C chemical shifts of the carbons close to the OH groups. Coupling constants and carbon and proton chemical shifts of compounds **1** and **2** are shown in Table II.

The assignment of the methyl peaks of the carbanion **2** was performed in the following novel way. The phase-sensitive NOESY spectrum of a mixture of **1** and **2** in DMF-d_7 was obtained. In this solvent the chemical shifts of the methyl groups were similar to those in DMSO. Negative cross peaks were due to NOEs, while positive ones were due to magnetization transfer by chemical exchange between **1** and **2**.[15] Correlation of plotted positive contours with known peaks of the methyl groups in **1** gave the assignment of the methyl groups in **2** (Figure 4).

Acknowledgment. We thank Docent Lars Baltzer for advice and assistance in connection with the NMR experiments and the Swedish Natural Science Research Council for financial support.

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(14) Reuben, J. *J. Am. Chem. Soc.* **1985**, *107*, 1756.

(15) Sanders, J. K. M.; Hunter, B. K. Reference 11, p 172.