

Hydrogen Bonding of a Hydroxy Proton to an Indenide Carbanion observed by N.M.R. and I.R. Spectroscopy. The Use of Cryptand to make the Alcohol Group Less Acidic than the Carbon Acid in Aprotic Solvents of Low Dielectric Constant

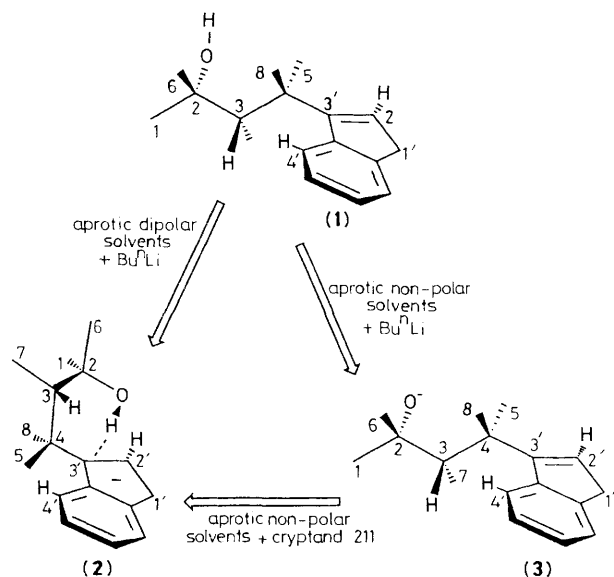
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The indene moiety in 4-(inden-3'-yl)-2,3,4-trimethylpentan-2-ol (**1**) is a stronger acid than the hydroxy group in dipolar aprotic solvents but the acidity is reversed in non-polar aprotic solvents; addition of cryptand makes the hydrogen-bonded carbanion (**2**) the most favoured species in all solvents.

In the mechanism of proton transfer reactions, hydrogen-bonded carbanions are postulated as intermediates. The investigation of hydrogen bonding of carbanions by hydroxy groups is difficult because the acidity of the carbon acids is normally too high to allow their conjugate anions to survive in the presence of OH groups.^{1,2} In earlier communications^{3a,b} we produced some evidence in support of intramolecular hydrogen bonding in carbanion (**2**) in dimethyl sulphoxide (DMSO), by n.m.r. and i.r. spectroscopy. DMSO is a very strong hydrogen bond acceptor, and for this reason other less polar solvents, which were weaker hydrogen bond acceptors, were investigated. The use of less polar solvents enhances the difference in hydrogen bond strength between the intramolecular hydrogen bond and the intermolecular hydrogen bond to the solvent. This is clearly observed by n.m.r. and i.r. spectroscopy.

The addition of BuLi to a solution of the precursor (**1**) in tetrahydrofuran (THF) gave an almost colourless solution, *i.e.*, the alkoxide (**3**) was obtained. In DMSO, the solution was strongly yellow-coloured owing to the presence of carbanion. Addition of cryptand 211 to the lithium alkoxide solution instantly made it strongly yellow-coloured. ¹H n.m.r. spectroscopy confirmed the presence of an indenide carbanion and alcohol, while no alkoxide could be observed. It is clear that the relative acidity of the OH group and the carbon acid is reversed by the addition of cryptand 211. It is suggested that the carbanion (**2**) and the alkoxide (**3**) are paired⁴ with Li⁺, and that the Li⁺ (**3**) pair is more stable than the Li⁺ (**2**) pair, because the alkoxide Li⁺ interaction is stronger than that of the indenide Li⁺. Cryptand 211 binding of Li⁺ separates the cation from the alkoxide and the indenide, respectively, and makes the anion (**3**) a stronger base than (**2**).



The carbanion (**2**) could be made not only in THF, but also in other non-polar solvents of lower dielectric constant like benzene and toluene, after the addition of cryptand 211 to the

Table 1. ¹H Chemical shift and stretching band of the OH proton in (**1**) and (**2**) in DMSO, THF,^a benzene,^a and toluene.^a

Solvent	¹ H Chemical shift ^b /δ		Stretching band ^c /cm ⁻¹	
	(1)-OH	(2)-OH	(1)-OH	(2)-OH
DMSO	4.02	3.61	3393	3316
THF	3.16	3.89	3469	3324
Benzene	1.29	4.53	3584	3310
Toluene	1.39	4.54		

^a An equivalent of cryptand 211 relative to the concentration of (**2**) was added to the solution. ^b The reference frequencies were set at δ 2.50 in [²H₆]DMSO, at δ 3.58 in [²H₈]THF, at δ 7.20 in [²H₆]benzene and at δ 2.30 in [²H₈]toluene. The chemical shift of the OH proton of (**1**) in THF, benzene, and toluene was obtained without any cryptand or carbanion present. The ¹H n.m.r. spectra were obtained in DMSO at 30 °C and in the other solvents at 21 °C. The concentration of the solutions was *ca.* 15 mM. ^c The i.r. spectra were obtained at 21 °C and at similar concentrations as in the ¹H n.m.r. experiments.

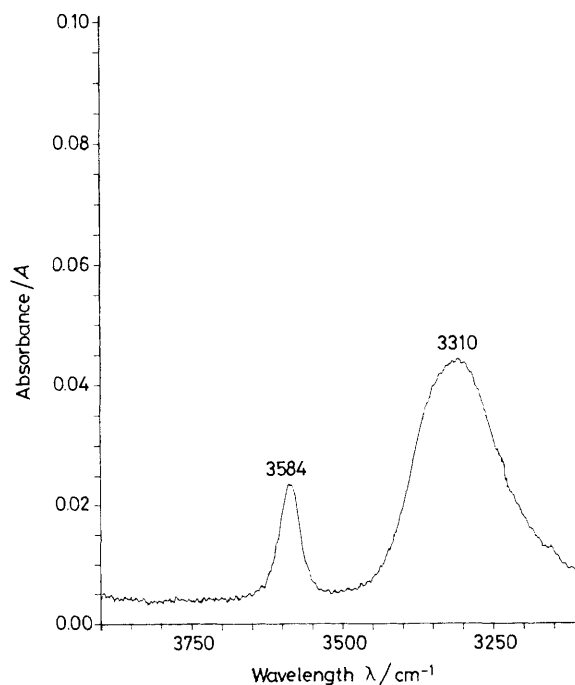


Figure 1. F.t.i.r. absorption spectrum of a mixture of (**1**) (8.7 mM) and (**2**) (7.7 mM) with cryptand 211 (10 mM) in benzene at 21 °C. The OH stretching band of (**1**) appears at 3584 cm⁻¹ and the stretching band of the OH group of (**2**), which is hydrogen bonded to the indenide carbanion, at 3310 cm⁻¹.

lithium alkoxide solution. These two solvents are weak proton acceptors and the OH proton of the precursor (**1**) will hydrogen bond weakly to the solvent. This is indicated by the high field ^1H chemical shift in benzene at δ 1.29, and the high frequency of the OH stretching band at 3584 cm^{-1} in the i.r. spectrum. Upon making the carbanion (**2**) in benzene, the OH proton, which now hydrogen bonds to the carbanion, resonated at δ 4.53 in the ^1H n.m.r. spectrum and the OH group vibrated at 3310 cm^{-1} ; *i.e.*, a shift to a lower field of 3.24 p.p.m. and a shift to lower frequency of 274 cm^{-1} (Table 1). The stretching band was both broader and more intense than that of the precursor (Figure 1).

Thus, intramolecular hydrogen bonding to the carbanion was observed in both dipolar and non-polar aprotic solvents that are either strong or weak hydrogen bond acceptors. The character of the hydrogen bond of the OH proton to the carbanion is essentially independent of the solvent, as the i.r. spectroscopy results show.

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