Nuclear Magnetic Resonance Spectra of Carbanions. VIII.[1] α-Picolyllithium

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The pmr spectra of the benzyl-type carbanions containing hetero atoms have not yet been reported as far as we know. We have recently observed the pmr spectra of α-picolyllithium in THF solutions. α-Picolyllithium was prepared from 6.35 mmol of α-picoline in contact with 6.05 mmol of phenyllithium in THF in a vacuum. A typical spectrum of α-picolyllithium is given in Fig. 1. One strong impurity signal is observed at 7.31 ppm; it is due to benzene. The other signals can be easily assigned by means of their intensities and structures except for some small impurity signals. The observed chemical shifts are given in Table 1, along with those of α-picoline and benzyllithium for comparison, taking the solvent peak at 1.79 ppm as a reference. The chemical shifts for the 0.22 and 0.58 mol/*l* solution of the carbanion were consistent within the limits of experimental error (±0.03 ppm). The coupling constants between the ring protons are $J_{34}=9.0$, $J_{35}=1.5$, $J_{36}=1.0$, $J_{45}=6.5$, $J_{46}=1.9$, and $J_{56}=5.5$ Hz, as evaluated from the first-order analysis for a 0.22 mol/*l* solution of the carbanion in THF. The data are compared with those of benzyllithium reported by Sandel and Freedman.[3] The ring protons of α-picolyllithium are more shielded than those of benzyllithium except for the 6-hydrogen, which is strongly affected by the nitrogen atom. The extra charge transferred from lithium to the pyridine ring in α-picolyllithium can be evaluated from the chemical shifts, using the procedures in a previous report.[4] The charges are -0.16_5, -0.15, -0.22, and -0.15 in units of the absolute value of the charge of an electron for the 3-, 4-, 5-, and 6-carbons respectively, taking picoline as the reference compound. There is a question of the magnitude of the proportional coefficient of the 10 ppm/electron, used for the charge estimation.[5] However, we can compare the extra charges transferred from lithium to the aromatic ring of the carbanions relatively. It is estimated that the more shielded the aromatic protons in the carbanions, the more stable the carbanions become. The extra charges are more transferred from lithium to the aromatic ring in α-picolyllithium than that in benzyllithium.[3] Therefore, the ionic nature of the metal-carbon bond in α-picolyllithium may be larger than that in benzyllithium, and α-picolyllithium may be more stable than benzyllithium. The methylene protons of α-picolyllithium are less shielded than the methyl protons of α-picoline. This tendency may be ascribed to the hybridization change in the α-carbon atom from sp^3 in α-picoline to near-sp^2 in α-picolyllithium, as was reported before in the α-methylstyrene dimer dianion.[4] The line width of the methylene proton signal is broader than the other ring proton signals in α-picolyllithium. Three reasons explaining this broadening may be considered. They are the nitrogen quadrupole relaxation effect, the coupling with ring protons, and the nonequivalency of the two methylene protons. The last reason seems to be most probable. Further studies are now in progress.

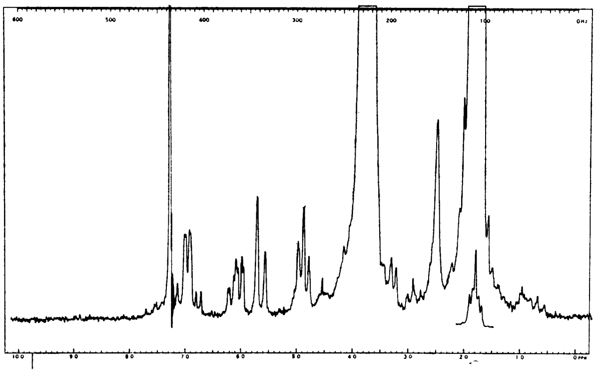

Fig. 1. A spectrum of a 0.58 mol/*l* α-picolyllithium in THF. Applied radio frequency increases from right to left near 60 MHz at a constant magnetic field.

Table 1. The proton chemical shifts of α-picolyllithium and the related compounds in THF at 60 MHz in ppm

Compound	Assignment				
	3-H	4-H	5-H	6-H	CH_2 or CH_3
α-Picolyllithium	5.68	6.08_5	4.87_5	6.92	2.53_5
Benzyllithium[a]	6.09	6.30	5.50	6.30	1.62[b]
α-Picoline	7.34_5	7.56	7.05_5	8.42	2.48_5

a) Ref. 3. b) Ref. 6.

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