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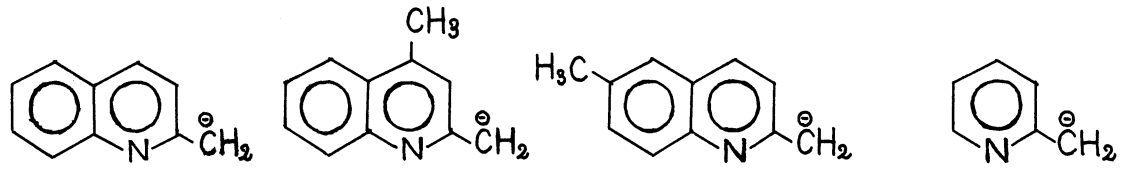
NMR STUDIES OF PICOLYL-TYPE CARBANIONS. III.[1),2)] QUINALDYLLITHIUM AND ITS METHYL DERIVATIVES

Kazuyori KONISHI, Yasuo ONARI, Shigeki GOTO, and Kensuke TAKAHASHI*
Mie Industrial Research Institute, Takajaya-komori-cho, Tsu 514
*Department of Industrial Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466

The proton magnetic resonance spectra of the title carbanions have been observed in tetrahydrofuran(THF) with lithium as a counter ion. The two methylene protons in these carbanions are nonequivalent at room temperature. This shows that the α-carbon in these carbanions is in a near-sp^2 configuration.

In our previous report, the carbanions produced by the reactions of methyl-substituted pyridines with n-butyllithium were studied.[1),2)] This study has been extended to the carbanions prepared from methyl-substituted quinolines in contact with n-butyllithium. These carbanions prepared are numbered from (I) to (III) as follows. (IV) was presented for comparison.



(I) (II) (III) (IV)

The procedures used in this study are similar to those described in the previous reports.[1),2)] Commercially available quinaldine, 2,4-dimethylquinoline and 2,6-dimethylquinoline were used after dried over CaH_2 and vacuum distilled. The chemical shifts were evaluated from the higher field peak of THF, used as an internal reference. This peak of THF was taken as 1.79 ppm from TMS.

The PMR data of the carbanions and the starting materials are given in Table 1. The results come from a first-order analysis. A typical spectrum of (I) is given in

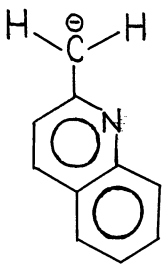
Table 1. The proton chemical shifts of the carbanions and the starting materials, in THF at 60 MHz and 35°C in ppm[a)]

Compound	Assignment							
	3-H	4-H	5-H	6-H	7-H	8-H	CH_2	CH_3
(I)	5.92	6.65_5	6.35_5	6.04	6.19	6.55	2.88,3.09	
(II)	5.88		6.58_5	6.13	6.38	6.74_5	2.87,3.06	
(III)	5.95	6.50_5	6.36		6.23_5	6.41	2.87,3.09	2.09
			(5'-H)	(6'-H)				
(IV)	5.64_5	6.06	(4.84)	(6.90)			2.54	
							2.45[b)],2.56[b)]	
Quinaldine	7.29_5	8.08_5	7.82	7.44	7.67	8.02_5		2.72
2,4-Dimethyl quinoline	7.12		7.82	7.40	7.64_5	8.00		2.65
2,6-Dimethyl quinoline	7.21_5	7.95	7.54		7.45_5	7.88		2.51,2.68
			(5'-H)	(6'-H)				
2-Picoline	7.16	7.57	(7.07)	(8.46)				2.48_5

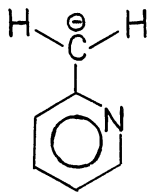
a) Errors are estimated to be within ±0.03 ppm. b) Measured at -25°C in 1,2-dimethoxyethane(DME).

Fig. 1(a). The signals at δ2.88 and 3.09 are attributable to the two methylene protons of the carbanion. The other signals can be assigned by means of their intensities and structures except for some small impurity signals. Figure 1(b) and (c) show typical spectra of (II) and (III), respectively. One strong peak observed at 5.37 ppm is impurity signal.

Although the methylene proton signal of (IV) appears as a singlet at room temperature, those of (I)~(III) appear as doublets; that is, the two methylene protons in (I)~(III) show magnetic nonequivalence at room temperature. This nonequivalence is explained by the restricted rotation around the bond between the heterocyclic ring and the α-carbon, caused by the resonance stabilization. Therefore the nonequivalence observed in (I)~(III) shows that these carbanions have the near-sp^2 configuration at the α-position. This result implies that the rotational barriers between the ring and the α-carbon in (I)~(III) are greater than that in (IV).



(I)



(IV)

The difference between the chemical shifts of the two methylene protons in (I)~(III) is about 0.2 ppm. This difference may be caused by the magnetic anisotropy of neighboring group. The magnitude of this chemical shift difference is similar to that between the two methylene protons of α-methylstyrene(about 0.25ppm). The coupling constant between the two methylene protons in (I)~(III) is about 2 Hz. This magnitude

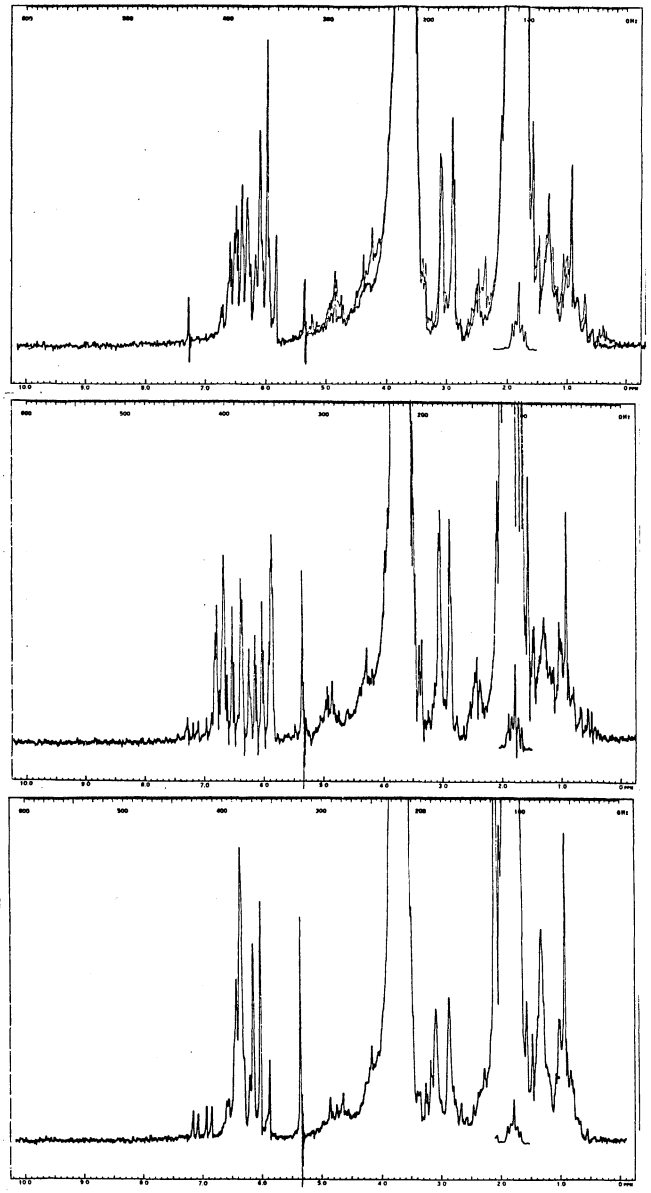


Fig. 1. PMR spectra of quinaldyl carbanions in THF at 60 MHz and 35°C ; (a) (I), (b) (II), and (c) (III).

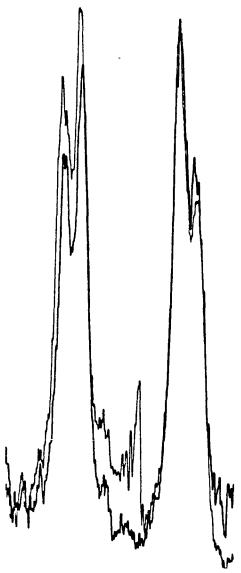
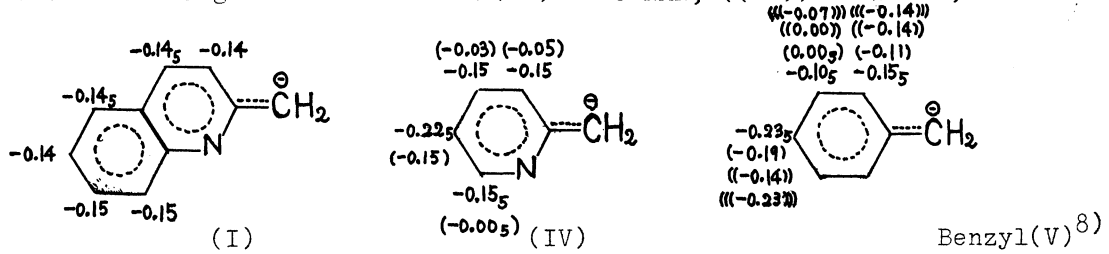


Fig. 1(d). An expanded spectrum of the methylene peaks of (II).

is similar to that of the geminal coupling constants of the vinyl compounds, and is different from those of the methane derivatives.[3),4)] This result also shows that the α-carbon atoms in these carbanions are in near-sp^2 configurations. A typical expanded spectrum of the methylene peaks is shown in Fig. 1(d).

The signals of the ring protons in these carbanions are shifted to higher field as compared with those in the starting materials. This arises from the extra charge delocalization to the aromatic ring in the carbanion.[5)] The extra charge distribution estimated from the chemical shift changes are given in Fig. 2, using the procedures in a previous report.[2)] The tendency of this distribution in the quinaldyl carbanions is similar to that in the picolyl carbanions. In this sense, the proton chemical shift is

Fig. 2. The relative charge distribution in the carbanions in units of the absolute value of the charge of an electron. ( )--^{13}C NMR, (( ))--LCAO-MO, ((( )))--SCF-MO



not an unfailing index of π-electron densities in the quinaldyl carbanions. On the other hand, the methylene proton peaks in these carbanions are deshielding with respect to the methyl proton peaks in the starting materials. As was pointed out previously,[2),6)] this deshielding of the methylene protons can be ascribed partly to the hybridization change of the α-carbon atom. If this interpretation is correct, it is interesting that the extent of the deshielding of the methylene protons in (I)~(III) is larger than that in (IV). The chemical shift difference between the methylene protons and the methyl protons are given in Table 2.

In short, these experimental results lead to the conclusion that the α-carbon atoms in (I)~(III) are nearer sp^2-hybridized as compared with that in (IV). Further studies are now in progress.

Table 2. The chemical shift difference, $\Delta\delta=\delta_{(CH_2)}^{\ominus}-\delta_{(CH_3)}$, in THF

Carbanion		Quinaldyl(I)	2-Picolyl(IV)	Benzyl(V)
Δδ(ppm)	^{1}H NMR	0.26_5	0.05_5	-0.08[a]
	^{13}C NMR		33.0[b]	31.3[c]

a. Ref. 7. b. in DME. c. Ref. 8.

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