CHEMISTRY LETTERS, pp. 169-170, 1982. © The Chemical Society of Japan 1982

^{15}N CHEMICAL SHIFTS OF 2,4,6-TRIMETHYLPYRIDINE AND ITS ANIONS[1)]

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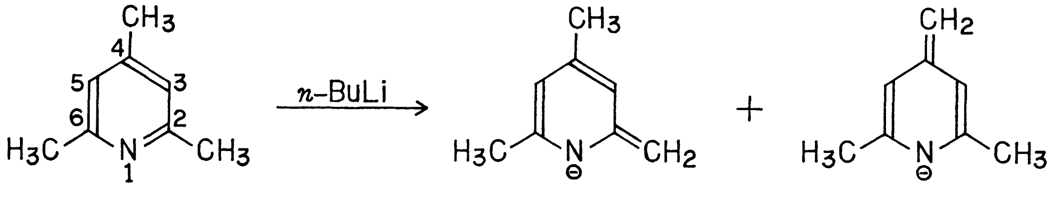
The ^{15}N chemical shifts have been observed for three enriched title compounds in diethyl-d_{10} ether by means of an INDOR technique. The shifts are discussed in terms of the electron densities on the ring nitrogens.

We have recently obtained the ^{15}N chemical shifts of the title anions. This is the first observation of the ^{15}N NMR parameters of the aromatic carbanions containing nitrogen, as far as we know.

The ^{15}N enriched anions, II and III, were prepared from enriched 2,4,6-trimethylpyridine, I, with butyllithium. The ^{15}N INDOR spectra were observed at 60.0 MHz with a Hitachi R-20B spectrometer by attaching a synthesizer and a hand-made digital sweep unit for irradiation of a second frequency(6.083 MHz). As has already been reported, I undergoes deprotonation to give II and isomerization takes place from the II to the thermodynamically more stable anion III.[2)] The conversion from II to III is faster in THF than in diethyl ether. Then the latter solvent is preferred to use for simultaneous observation of the spectra of II and III at ambient temperature.



I II III

A ^{1}H NMR spectrum of I-III is shown in Fig. 1. The signal at 6.68 ppm is attributable to the ring protons of I remaining after the reaction. The ^{15}N and ^{1}H NMR data for I-III are given in Table 1.

The ^{15}N resonances of II and III are found upfield about 100 ppm from that of I. The ring protons and carbons also show upfield shifts, except for the 2-C of II and the 4-C of III.[2)] In all the aromatic ring atoms of the anions, the remarkable upfield shifts are observed at the 1-, 3-, and 5-positions. These upfield shifts are explained by the excess-charge delocalization into the aromatic ring, leading to the resonance stabilization. Further, the nitrogen shift of III is upfield from that of II. This upfield shift is also ascribed to an increase in the electron density on the ring nitrogen. Therefore, the ^{15}N chemical shifts for I-III seem to be correlated with the electron densities on the ring nitrogens. In fact, their chemical shifts decrease with the increasing electron densities calculated using the CNDO/2 MO method, as given in Table 1. Further studies along this line are now in progress.

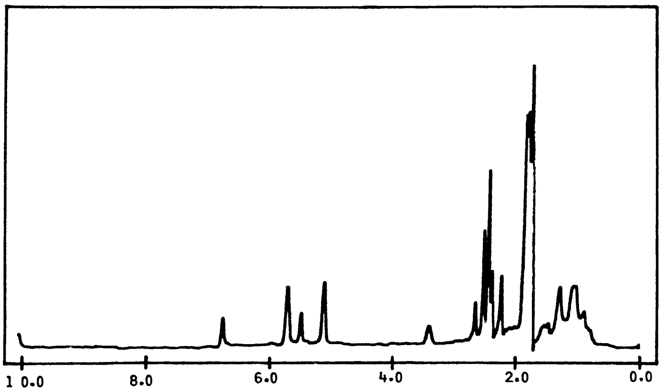


Fig. 1. ^1H spectrum of I, II, and III in diethyl-d_{10} ether at 60 MHz.

Table 1. The nitrogen and proton chemical shifts of 2,4,6-trimethylpyridine and its anions, in ppm[a)]

Species	Assignment							
	1-N	3-H	5-H	2-CH_3	4-CH_3	6-CH_3	2-CH_2	4-CH_2
I	308.9(5.202)[b)]	6.68 (1.3)[c)]	6.68 (1.3)	2.36 (3.0)	2.18 (~ 0)	2.36 (3.0)	---	---
II	206.3(5.317)	5.66 (1.3)	5.06 (1.4)	---	1.71 (~ 0)	1.81 (2.7)	2.44 (4.8)	---
III	199.5(5.339)	5.43 (1.3)	5.43 (1.3)	1.78 (2.5)	---	1.78 (2.5)	---	2.59 (~ 0)

a) The nitrogen chemical shifts are referred to an external enriched liquid nitromethane as suggested in Ref. 3 and then the values are converted to those from the anhydrous liquid ammonia at 25 °C by taking δ380.23 for nitromethane, and the proton chemical shifts are referred to an external neat TMS signal. b) The values in parentheses are the total electron densities on the ring nitrogens. c) The values in parentheses are the coupling constants between nitrogen and proton in Hz.

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(Received November 16, 1981)