

Isolation and Characterization of Crystalline σ -Complexes from Organolithium Compounds and Pyridine Derivatives

By C. S. GIAM* and J. L. STOUT

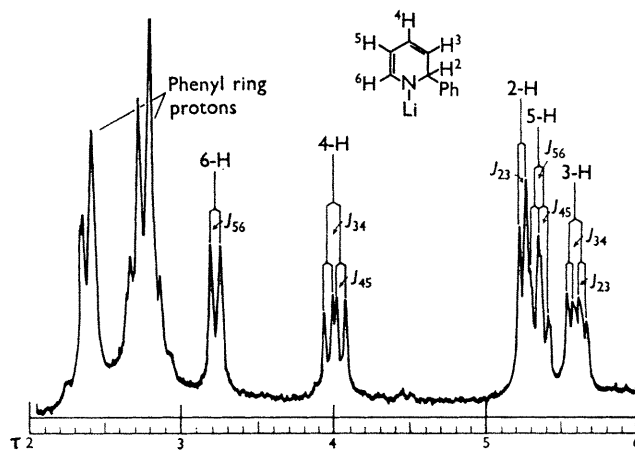
(Department of Chemistry, Texas A & M University, College Station, Texas, 77843)

ALTHOUGH it has been postulated¹ that nucleophilic aromatic substitutions of pyridines by organolithium compounds and alkali amides² proceed *via* an addition-elimination mechanism involving an intermediate σ -complex, there has been little direct evidence for this.³ Recently, it was reported⁴ that ethereal solutions of *n*-butyl-lithium and pyridine gave a ¹H n.m.r. spectrum consistent with structure (1a) but such adducts have never been isolated. We now report the isolation and characterization of a series of such intermediates.

	<table border="0"> <tr> <td>R¹</td> <td>R²</td> <td>R³</td> <td>R⁴</td> </tr> <tr> <td>(1a) Buⁿ</td> <td>H</td> <td>H</td> <td>H</td> </tr> <tr> <td>(1b) Ph</td> <td>H</td> <td>H</td> <td>H</td> </tr> <tr> <td>(1c) Ph</td> <td>H</td> <td>Bu^t</td> <td>H</td> </tr> <tr> <td>(1d) Ph</td> <td>Me</td> <td>H</td> <td>H</td> </tr> <tr> <td>(1e) Ph</td> <td>Me</td> <td>H</td> <td>Me</td> </tr> </table>	R ¹	R ²	R ³	R ⁴	(1a) Bu ⁿ	H	H	H	(1b) Ph	H	H	H	(1c) Ph	H	Bu ^t	H	(1d) Ph	Me	H	H	(1e) Ph	Me	H	Me
R ¹	R ²	R ³	R ⁴																						
(1a) Bu ⁿ	H	H	H																						
(1b) Ph	H	H	H																						
(1c) Ph	H	Bu ^t	H																						
(1d) Ph	Me	H	H																						
(1e) Ph	Me	H	Me																						

Pyridine was added carefully to an ice-cold solution of lithium bromide-free phenyl-lithium⁵ in ether, to give a yellow precipitate which was washed with dry ether, and taken up in tetramethylethylenediamine. This solution gave a 10H n.m.r. spectrum (Figure). The intensities, positions, and multiplicities of the lines in the spectrum could be assigned unambiguously⁶ to structure (1b); the resonances centered at τ 2.37 and 2.74, respectively, were assigned to the 5 phenyl-ring protons and the remaining 5 pyridine-ring protons were assigned as listed in the Table. Coupling constants between adjacent pyridine-ring protons were

in the ¹H n.m.r. spectrum of the 4-*t*-butylpyridine adduct (1c)]. Good elemental analyses of the adduct (1b) were precluded by its moisture-, oxygen-, and heat-sensitive nature. Fortunately, a derivative (2-phenylpyridine) was obtained in excellent yields (80%) when an ethereal solution of the adduct was treated with dry oxygen. There was little doubt that the σ -intermediate (1b) was isolated.



FIGURE

Similarly, other organolithium-pyridine adducts were isolated and the relevant chemical shifts are summarized in the Table.

Chemical shifts of pyridine-ring protons of σ -complexes in tetramethylethylenediamine at 100 MHz.

Adduct	τ -values					(c. sec.)			
	2-H	3-H	4-H	5-H	6-H	J_{23}	J_{34}	J_{45}	J_{56}
(1b)	5.22	5.57	3.99	5.32	3.21	4.40	8.00	5.75	5.75
(1c)	5.22	5.57		5.32	3.33	4.12			6.50
(1d)	5.23		4.37	5.69	3.48			5.50	6.00
(1e)	5.27		4.42		3.69				

measured directly from the spectrum and were helpful in the correct assignment of the resonance lines. The small (or negligible) coupling constants of the more distant protons could not be accurately determined but they did not hinder the assignment. The correctness of the assignment was further confirmed by spin-spin decoupling experiments[†] and by comparisons of ¹H n.m.r. spectra of adducts formed from suitable pyridines [*e.g.* the resonance of 4-H was absent

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¹ K. Ziegler and H. Zieser, *Ber.*, 1930, 1847.

² R. A. Abramovitch, F. Helmer, and J. G. Saha, *Canad. J. Chem.*, 1965, 43, 725.

³ R. A. Abramovitch and G. A. Poulton, *Chem. Comm.*, 1967, 275.

⁴ G. Fraenkel and J. C. Cooper, *Tetrahedron Letters*, 1968, 1825.

⁵ Prepared from diphenylmercury and lithium; a slight excess of phenyl-lithium was used. Other preparations of phenyl-lithium could also be used (See R. A. Abramovitch and C. S. Giam, *Canad. J. Chem.*, 1963, 41, 3127.)

⁶ J. W. Emsley, J. Feeny, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, 1965, vol. 1 and 2.