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N-LITHIO DERIVATIVES OF α,β UNSATURATED AMINO IMINES

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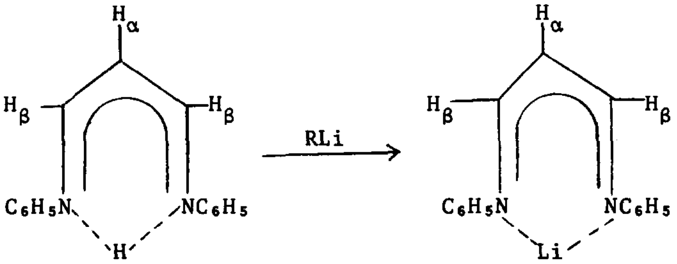
N-lithio derivatives of I and some analogues were prepared[1] by the reaction of the parent amino imine with alkyl lithium (1:1 mole ratio). Physical properties of these compounds have been investigated to determine whether the lithium atom is an effective part of the π system.



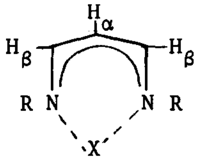
The N-lithio derivatives were very soluble in tetrahydrofuran and soluble in nonpolar solvents such as hexane. This contrasts with the parent amino imines which were slightly soluble in tetrahydrofuran and insoluble in hexane.

The nmr spectral data of a few of these compounds is shown in Table 1. Tetrahydrofuran was used as solvent and the chemical shifts are quoted from the strongest absorption of the O-methylene protons of the solvent. As we were interested in chemical shift differences of the lithio compound from the parent compound and as dilute solutions were used, this was considered a suitable standard.

U. V. spectra of the amino imines, their hydrochlorides and the N-lithio derivatives are shown in Table 2. Because of the moisture sensitivity of the N-lithio derivatives extinction coefficients were not obtained. Hydrolysis of the solutions used for determining λ_{max} indicated that the

Table 1

Chemical Shifts of



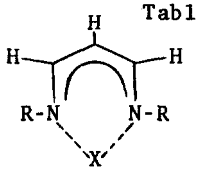
Compounds[*]

Compound	H_β(c/s)	H_α	$J_{H_\alpha H_\beta}$	Phenyl	Other
R=C_6H_5-; X=H (I)	-251	-72	7.5	-213	
R=C_6H_5-; X=Li (II)	-237	-54	6.5	-206	
R=p$CH_3C_6H_4$-; X=H	-248	-74	7.0	-206	pCH_3 + 81
R=p$CH_3C_6H_4$-; X=Li	-232	-47	6.5	-197	pCH_3 + 83
R=m$CF_3C_6H_4$-; X=H	-258	-73	8.5	-225	
R=m$CF_3C_6H_4$-; X=Li	-241	-61	6.5	-217	
R=$C_6H_4CH_2$-; X=H (H_β = CH_3)	-	-58	-	-215	-CH_2- -49 CH_3(β position) (not observed)
R=$C_6H_4CH_2$-; X=Li (H_β = CH_3)	-	-33	-	-215	-CH_2- -63 CH_3(β position) (not observed)

[*] Dilute solutions in tetrahydrofuran, chemical shift measured from strongest peak in the -CH_2-O region.

Table 2

U. V. Spectra of



Compounds in Tetrahydrofuran Solution[*]

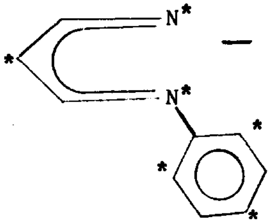
R	λ_{max} (nm) X = H	X = Li	Hydrochloride Derivative
C_6H_5	366	370	384
p$CH_3C_6H_4$-	376	382	394
m$CF_3C_6H_4$-	360	(364)[§]	381

[*] Spectra taken in 0.5 mm cells with freshly distilled tetrahydrofuran (from calcium hydride).

[§] Sample partially hydrolysed (large shoulder at 360 nm).

extinction coefficients were roughly the same as the parent amino imines.

Holm[2] has carried out simple Huckel calculations on the mono anion of these systems



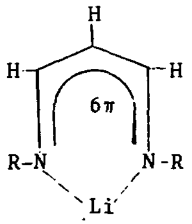
These calculations indicated large spin densities at the starred positions and much smaller spin densities at the other positions. This was borne out experimentally by nmr contact shifts of the nickel complexes.

Although we do not regard the N-lithio derivatives as anions it might be expected that any large increase in electron density would be observed at the 'para' (α) position in the system.

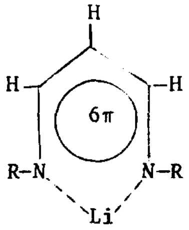
The nmr results in Table 1 indicated that, in general, larger changes in chemical shift were observed for the α protons than the β protons when the bridging hydrogen was substituted by lithium (ΔH_α = 18 c/s, ΔH_β = 14 c/s for I and II). The m-CF_3 compound did show the opposite effect (ΔH_α = 12 c/s, ΔH_β = 17 c/s). Also there was a decrease in the coupling constant $J_{\alpha\beta}$ in the N-lithio derivatives. These chemical shift changes are no greater than observed in the aryl lithium compounds.[3] Also the reduction in coupling constant is similar to that observed in aryl lithium compounds. Thus it appears that the substitution of lithium for hydrogen in this system has only as much effect as changing from benzene to phenyl lithium. In phenyl lithium it was observed that there was a large shift downfield for the ortho protons. Although in these systems there are no 'ortho' protons, in one compound, 2-benzylamino-4-benzylimino-2-pentene, there is a CH_2 group attached to the nitrogen atoms. These methylene protons are shifted downfield by 13 c/s in the N-lithio derivative.

The U. V. spectra show small shifts to lower energy as was observed for phenyl lithium. The changes in energy do not seem sufficient to postulate an involvment of the lithium atom in the conjugation. Much larger shifts were observed on protonation of the system.

It appears from the above evidence that the N-lithio derivatives of these α,β unsaturated amino imines favour structure III rather than structure IV.



III



IV

A similar conclusion was reached by Daltrozzo and Feldman[4] but no experimental evidence was produced.

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