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# THE REACTIONS OF α,β UNSATURATED AMINO IMINES WITH ALKYL LITHIUM COMPOUNDS

Keith J. Fisher

Department of Chemistry, University of Wisconsin, Madison, Wisconsin, U.S.A.

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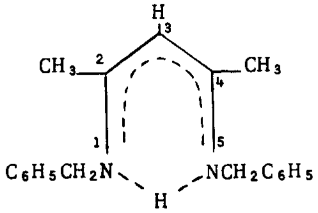
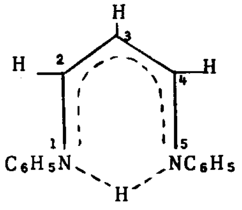
A 'non-classical' aromatic structure was proposed by Dorman[1] for 2-benzylamino 4-benzylimino-2-pentene(I) Malondialdehydedianil(II) and some close analogues were shown to have similar structures.[2] The main evidence for these structures was obtained from the nmr spectra.

(I)





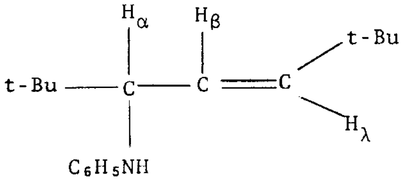
(II)

Holm[3] prepared nickel complexes of these compounds by first preparing the lithium compound and then reacting these, in situ, with tetraethylammonium tetrabromonickelate. It was considered worthwhile investigating the lithium complexes and other metal derivatives to find their influence upon the π system. While carrying out reactions of these compounds with alkyl lithiums it was noted that a greater than 1:1 mole ratio of amino imine to alkyl lithium caused cleavage of the amino imine.

The reaction of one mole of n-butyl lithium with one mole of I or II (or derivatives of II) in tetrahydrofuran at -78° C gave the N-lithio derivative. These compounds are highly reactive. The reaction with water gave the parent amino imine. The N-lithio derivatives were very soluble in tetrahydrofuran (the parent amino imines were insoluble or of limited solubility) and soluble in non polar solvents. The nmr spectra in tetrahydrofuran were similar to the parent compounds, indicating that a similar structure was retained. For example the N-lithio derivative of I gave a singlet for the benzyl methylene protons consistent with two equivalent nitrogen atoms as was found in parent amine. Chemical shift changes (especially for the hydrogen at position 2) were observed, these will be discussed in a future publication.[4]

II and derivatives are bright yellow crystalline compounds whereas the lithium compounds in tetrahydrofuran solution were red. U.V. and visible spectra have not yet been obtained because of the sensitivity to moisture and high extinction coefficients of the bands.

The reaction of t-butyl lithium with II, at room temperature for 24 hours, in a 4:1 mole ratio gave a yellow solid insoluble in the hexane solvent. This solid is very reactive and so far attempts to characterize this solid using physical techniques have been unsuccessful. The solid was reacted with water and gave two major volatile products. These products were aniline (∿35% yield) and 1,3-di-t-butylallylaniline (∿30% yield).



These compounds were identified by elemental analysis, infrared and nmr spectra.*

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* Di-t-butylallylaniline, nmr ($CCl_4$ solution, ppm $\delta$); t-butyl 0.98, 0.97 (two types); phenyl o- and p- 6.56 m- 7.05; $CH_\alpha$ 3.43 (broad doublet, N-H appears to be at the same position); $CH_\beta$ and $CH_\alpha$ 5.47 (complex pattern). ir ($cm^{-1}$)(neat liquid) 3440 (N-H)(m) 1603(vs) 1500(vs) 743(vs) Similar to the spectrum of allylaniline.

* Di-n-butylallylaniline, nmr ($CCl_4$ solution, ppm $\delta$); n-butyl (3 broad complex bands) ∿0.90, 1.40, 2.00; phenyl o-p 6.56, m- 7.07; $CH_\alpha$ 3.7 (broad) NH 3.35 (broad disappears on deuteration); $CH_\beta$ and $CH_\alpha$ 5.42 (complex pattern). ir ($cm^{-1}$)(neat liquid) 3420(m) 1605(vs) 1505(vs) 745(vs) 690(vs) Similar to the spectrum of allylaniline.

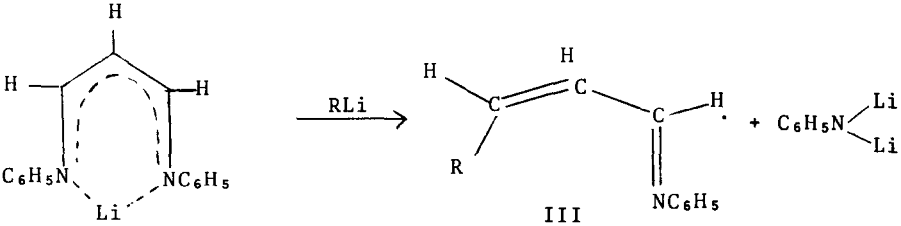
A similar reaction was obtained with n-butyl lithium and II under identical conditions. The products obtained were aniline and 1,3-di-n-butylallylaniline.[*]

Titrations of the water soluble base produced when the yellow solid (from the reaction of t-butyl lithium with II) was reacted with excess water indicated that there were three lithium atoms present per mole of amino imine initially used.

The reaction of n-butyl lithium with II (tetrahydrofuran solvent), at 0° C for 24 hours, in a 2:1 mole ratio gave a brown solution. Subsequent derivatization with water gave only one volatile product, aniline. Derivatizing with methyl iodide gave dimethyl aniline (∿25%).

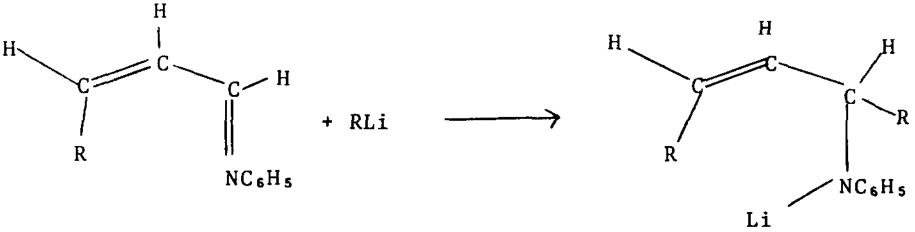
In both reactions a brown polymer was obtained after distillation of the aniline or dimethyl aniline.

It appears that a second mole of alkyl lithium reacts with the N-lithio derivative of the amino imine causing cleavage of a C-N bond.



III

In the presence of excess alkyl lithium addition across the C=N bond in III might take place.



The addition of alkyl lithium compounds across C=N bonds is quite well known.[5]

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## References

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