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EVIDENCE FOR A SINGLE ELECTRON TRANSFER MECHANISM IN THE REDUCTION OF AROMATIC NITROGEN HETEROCYCLES WITH MAIN GROUP METAL HYDRIDES AND DIHYDROPYRIDYL METAL COMPLEXES.

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SUMMARY: Direct spectroscopic (EPR) evidence is presented to support a single electron transfer mechanism to describe the reactions of various simple and complex hydrides of the main group elements and dihydropyridyl metal complexes with aromatic nitrogen heterocyclic compounds.

As part of our studies on the probable involvement of single electron transfer (SET) in reactions of organometallic and metal hydride compounds of main group elements with various organic substrates,[1-4] we have recently reported the involvement of a SET pathway in the reduction of polynuclear aromatic hydrocarbons by simple and complex metal hydrides.[4] In view of these recent findings, we decided to investigate the possibility of a similar pathway in the reduction of aromatic nitrogen heterocycles by the same reagents.

In the present study we employed typical simple and complex metal hydrides of the main group elements e.g., $LiAlH_4$, AlH_3, MgH_2 and $LiAl(OBu^t)_2H_2$ in addition to some dihydropyridyl metal complexes. The dihydropyridyl metal complexes: $LiAl(PyH)_4$, $Al(PyH)_3$ and $Mg(PyH)_2$ (where PyH = 1,2- or 1,4-dihydropyridyl-) where obtained by the reactions of pyridine with the corresponding metal hydrides.[5-7] In the formation of these reagents, hydride ion attack on the pyridine ring was considered by previous workers to take place via a polar mechanism. In view of the possible involvement of a SET mechanism in these reactions, we re-examined the reactions of several hydrides with pyridine and found that either none or only a trace amount of radical intermediate could be detected by EPR. If an electron transfer mechanism is operative, the non-detectibility of the radical intermediate was probably due to (a) the low persistence of the pyridyl radical; or (b) the rapid coupling of the pyridyl radical with the hydrogen atom. Since (b) is bound to be dependent on the steric requirement of the hydride reagent as well as the substrate and the reactivity of the metal hydride,[2,3] we decided to study the reactions of metal hydrides of variable reactivity with sterically bulky aromatic nitrogen heterocycles, such as, 1,10-phenantholine, 2,2'-bipyridine and isoquinoline. Indeed we have obtained significant concentrations of radical intermediates in these reactions and a preliminary account of these results is presented here.

When $LiAlH_4$ was dissolved in THF and allowed to react with equimolar amounts of 1,10-phenanthroline, 2,2'bipyridine and isoquinoline in THF at room temperature, dark colored solutions formed within a few minutes. These solutions showed only weak EPR spectra, however, the reactions resulted in the formation of reduction products in quantitative yields within one hour. Both 1,2-dihydro (kinetic product) and 1,4-dihydro (thermodynamic product) were formed in the case of 1,10-phenanthroline and 2,2'-bipyridine whereas in the case of isoquinoline only the 1,2-dihydro product was formed. However, when excess amounts of the heterocyclic compounds [2-4 fold excess] were treated with $LiAlH_4$, much higher amounts of radical intermediates were observed (radical conc. 1-10%). Thus it appears that intermediate hydride complexes $[LiAl(ArH_2)_nH_{4-n}]$ formed in these reactions (eq. 1) react with an excess of the heterocyclic compound at a much slower rate and thus the radical intermediates can be observed.

$$LiAlH_4 + n(ArH) \longrightarrow LiAl(ArH_2)_nH_{4-n} \qquad (1)$$

(where ArH = 1,10-phenanthroline, 2,2'-bipyridine or isoquinoline and n = 1,2 or 3)

The above results encouraged us to study the reactions of less reactive hydrides such as $LiAlH_2(OBu^t)_2$ and $LiAlH(OBu^t)_3$ with the same heterocyclic compounds in the hope that significantly higher concentrations of the radical intermediates might be observed. Indeed, these hydrides reacted with all of the heterocyclic compounds above at a much slower rate than comparable reactions using $LiAlH_4$. In every case higher concentrations of radical intermediates (3-27%) were detected (Table 1). Typically, when $LiAlH_2(OBu^t)_2$ was allowed to react with 2,2'-bipyridine in THF in 1:1 ratio (conc. 0.01M in each reagent) at room temperature, a deep violet-red color developed within a few minutes, the intensity of which increased continuously for several days. The solution showed a complex EPR spectrum which consisted of several well resolved lines (Fig. 1). The intensity of the signal increased steadily with time and after about 2 days was estimated to be ≈27% (based on starting material). Reduction product (1,2- and 1,4-dihydro-2,2'-bipyridine) was formed slowly throughout the course of the reaction. Interestingly, the radical intermediate was observed even after a much longer period (one month) which suggested that the radical pair intermediate (A) formed in this reaction according to Scheme 1 in addition to forming reduction product (B), underwent dissociation to give the free radical anion which stayed in solution for at least one month. Indeed the spectrum (Fig. 1) is identical to the spectrum of 2,2'-bipyridine radical anion formed by the reduction of 2,2'-bipyridine with lithium metal in THF. This result was not surprising considering the results

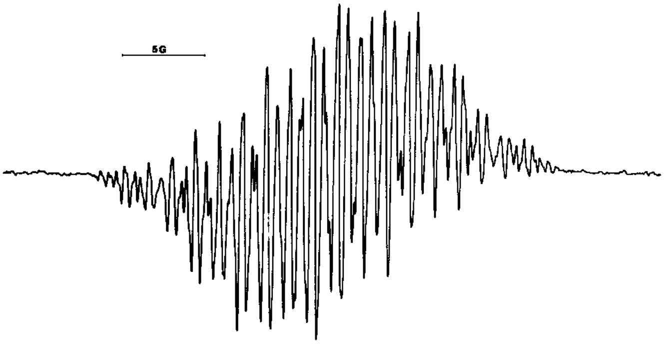
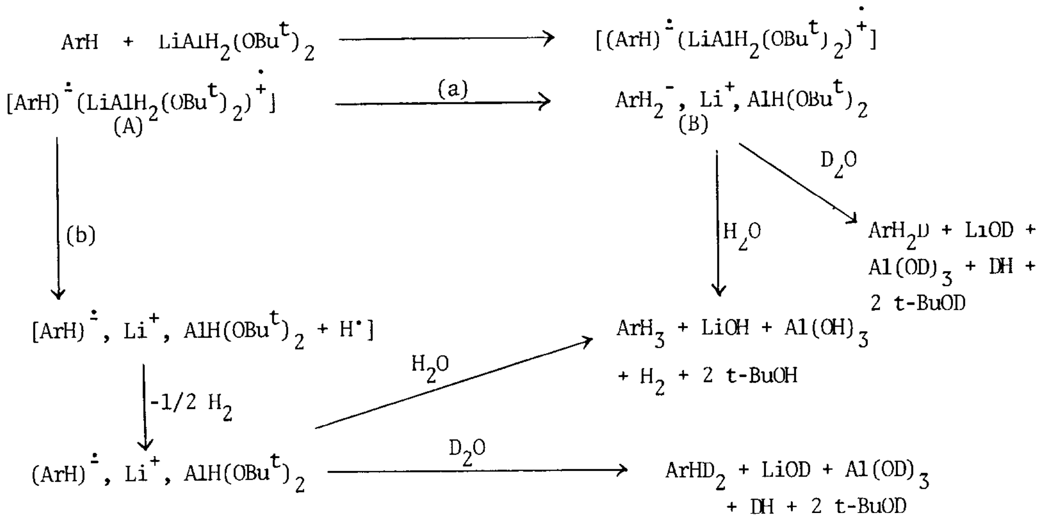


Figure 1: EPR spectrum of the radical intermediate formed in the reaction of $LiAlH_2(OBu^t)_2$ with 2,2'-bipyridine in THF at room temperature.

obtained earlier in the reaction of $LiAlH_4$ with polynuclear hydrocarbons (ArH) where a similar partial dissociation of the radical pair $(ArH)^{\cdot -}(LiAlH_4^{\cdot +})$ resulted in the formation of the radical anion $(ArH^{\cdot -}, Li^+)$[4].

SCHEME 1



ArH = aromatic nitrogen heterocycle

Formation of the radical anion was further supported by hydrolysis studies. When the reaction mixture was hydrolysed by D_2O both ArH_2D and $ArHD_2$ were formed. Similarly, when the same reaction was carried out employing $LiAl(OBu^t)_2D_2$ and hydrolysed with H_2O, again a mixture of ArH_2D and $ArHD_2$ were formed. These results indicate that (A) results in the formation of both (B) and (C). Reactions of these same heterocyclic compounds with various other metal hydrides and dihydropyridyl metal complexes gave variable amounts of radical intermediates and their amounts are given in Table 1.[8]

TABLE 1

Estimation of Radical Intermediate in the Reaction of Aromatic Nitrogen Heterocycles with Metal Hydrides and Dihydropyridyl Metal Complexes in THF.

Reagent	App. Conc. of Substrate (Molarity)	Ratio of Reagent/ Substrate	% Radical in the Reaction with Substrate		
			1,10-Phenanthroline	2,2'Bipyridine	Isoquinoline
$LiAlH_4$	0.01	1:1		trace	trace
$LiAlH_4$	0.01	1:2	<1	≈1	trace
$LiAlH_4$	0.02	1:4	3.4	9.8	1.2
$LiAlH_2(OBu^t)_2$	0.015	1:1	3.7	18.5	
$LiAlH_2(OBu^t)_2$	0.02	1:2	7.4	27.3	3

Table 1 (Con't)

Reagent	App. Conc. of Substrate (Molarity)	Ratio of Reagent/ Substrate	% Radical in the Reaction with Substrate		
			1,10-Phenanthroline	2,2'-Bipyridine	Isoquinoline
$LiAlH(OBu^t)_3$	0.02	1:1	7.5	2.8[b]	5.2
$LiAl(Py)_4$	0.02	1:1	≃1	≃1	trace
$LiAl(Py)_4$	0.02	1.2	2.2	4.3	≃1
AlH_3	0.01	1:1	≃1	1.2	trace
AlH_3	0.015	1:2	3.0	7.2	2
MgH_2	0.01	c	1	1.4	1
$Al(Py)_3$	0.015	1:2	4.2	9.9	2.9
$Mg(Py)_2$	0.02	c	<2	3.7	<1

[a] Concentration of each radical was estimated from its EPR spectrum. Values are within ±5%.

[b] Radical concentration was measured after 2 weeks while the intensity was still increasing slowly.

[c] Ratio of the reagent to substrate could not be measured (in solution) due to the insoluble (or partially soluble) nature of the reagent.

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