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REACTIONS OF PHENYLLITHIUM WITH LITHIUM ALUMINUM HYDRIDE IN DIETHYL ETHER

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Summary

Reactions of phenyllithium with $LiAlH_4$ in diethyl ether have been studied in detail. Lithium hydride, as an insoluble solid, and $LiAlPh_nH_{4-n}$ (where $n = 2$ or 3) in solution, are formed when the PhLi to $LiAlH_4$ ratio is 2/1 and 3/1. However, Li_3AlH_6 is formed when $LiAlH_4$ is added to an equimolar solution of PhLi in diethyl ether. The integrity of the products have been established by IR, NMR and X-ray powder diffraction pattern.

Introduction

We have been interested for some time in the preparation of complex metal hydrides and studies of reactions which lead to such compounds. In this connection, we have reported not only on the preparation of new complex metal hydrides, such as $KMgH_3$ [1], Li_2ZnH_4 [2], $LiCuH_2$ [3], and others, but have also been interested in studying, as carefully as possible, fundamental reactions involving complex metal hydrides so that the chemistry of these compounds might be both understood and utilized. We have recently carried out the reaction of $LiMgMe_3$ with $LiAlH_4$ with the hope of preparing $LiMgH_3$ in much the same manner as we have previously prepared $LiZnH_3$ by the reaction of $LiZnMe_3$ with $LiAlH_4$ (eq. 1). Unfortunately, the reaction of $LiMgMe_3$ with $LiAlH_4$ produced a considerable amount of LiH and MgH_2, indicating that $LiMgMe_3$ dissociates to MeLi and Me_2Mg which on reaction with $LiAlH_4$ produce LiH and MgH_2, respectively (eq. 2).

$$LiZnMe_3 + LiAlH_4 \rightarrow LiZnH_3 + LiAlMe_3H \qquad (1)$$

$$LiH + MgH_2 \xleftarrow{LiAlH_4} MeLi + Me_2Mg \rightleftharpoons LiMgMe_3 \xrightarrow{LiAlH_4} LiMgH_3 \qquad (2)$$

In view of this result, we decided to prepare a more stable "ate" complex such as $LiMgPh_3$, which on reaction with $LiAlH_4$ would produce $LiMgH_3$. According to earlier reports [4], $LiMgPh_3$ is a stable compound. However, if some dissociation takes place in diethyl ether to give PhLi and Ph_2Mg, we should be able to detect the LiH and MgH_2 that are formed. On the other hand, if no dissociation takes place, we should be able to isolate pure $LiMgH_3$. We have studied the reaction of Ph_2Mg with $LiAlH_4$ in detail and find that MgH_2 is formed under all the conditions studied [5]. However, on studying the reaction of PhLi with $LiAlH_4$ under a variety of conditions, we have found some unusual results.

Experimental

Apparatus

Reactions were performed under dry nitrogen at the bench or in a glove box equipped with a recirculating system using manganese oxide to remove oxygen. Infrared spectra were obtained on a Perkin—Elmer 621 spectrophotometer using KBr and CsI liquid or mull cells. NMR spectra were recorded in ether solution on a Varian-A60 spectrometer. The X-ray powder diffraction pattern of all products were obtained on a Philips—Norelco X-ray unit using a 114.6 mm camera with nickel filtered Cu-K_α radiation. The samples were sealed in a 0.5 mm capillary and exposed to X-rays for 6 h. The "*d*" spacings were read on a precalibrated scale equipped with a viewing apparatus. Line intensities were estimated visually.

Analyses

Gas analyses were accomplished by hydrolysis of samples with HCl on a standard vacuum line equipped with a Toepler pump. Aluminum was determined by adding an excess of EDTA and back-titrating with standard zinc acetate at pH 4 in 50% ethanol with dithizone as an indicator. Lithium was determined by flame photometry. Phenyl groups present in the complexes were determined as benzene by hydrolyzing the samples with water and analyzing the filtrate by GLC using an SE 30 column at 70°C. Mesitylene was used as the solvent and hexanol was used as the internal standard.

Materials

Solvents were distilled from $LiAlH_4$ (ether) or $NaAlH_4$ (THF, benzene and mesitylene) immediately prior to use. Phenyllithium was prepared by the reaction of iodobenzene in benzene with n-butyllithium in hexane. The solid product was dissolved in ether, recrystallized at —78°C, redissolved in freshly distilled ether and standardized by Watson—Eastham titration. It has been observed that PhLi cleaves ether at room temperature to give the product $Li_2(OEt)Ph$ after 24 h. Ether cleavage was avoided by storing the solution at —15°C prior to use.

Triphenylaluminum was prepared by refluxing a mixture of Ph_2Hg and aluminum chips in toluene for 40 h and filtering the resulting hot mixture through glass wool using nitrogen pressure [6]. The product was recrystallized from hot toluene and dried under reduced pressure (0.05 mmHg) for 1 h at 60°C.

Lithium aluminum hydride was obtained from Ventron, Metal Hydride Division. A solution was prepared by refluxing $LiAlH_4$ in ether overnight. The solution was filtered through a medium glass-fritted funnel using dried Celite Analytical Filter-Aid (Johns—Mansville). The clear solution was standardized by aluminum analysis.

Lithium tetraphenylaluminate ($LiAlPh_4$) was prepared by the addition of PhLi solution in ether to Ph_3Al in ether with continuous stirring. A viscous, liquid layer separated from the ether and crystallized overnight. The resulting white solid is soluble in THF but insoluble in diethyl ether. Analysis of the THF solution gave the following results: Found: Li/Al/Ph 1.00/1.06/4.10. $LiAl(C_6H_5)_4$ calcd.: Li/Al/Ph 1.0/1.0/4.0. The X-ray powder diffraction pattern for $LiAlPh_4$ is given in Table 1.

Reaction of PhLi with $LiAlH_4$ in diethyl ether in 1/1 ratio

To a well-stirred solution of 8.0 mmol of PhLi in 20 ml of diethyl ether at 0°C was added dropwise an ether solution of 8.0 mmol of $LiAlH_4$ in 30 ml of ether. Reaction was instantaneous and a precipitate separated from the solution. The reaction mixture was stirred for 15 min at 0°C and then at room temperature for 1 h. The insoluble solid was filtered, washed with diethyl ether and dried under vacuum. Analysis of the filtrate revealed that it contained Li/Al/H/Ph in molar ratios of 1.02/1.00/1.95/2.01. The filtrate contained 4.05 mmol (50%) of the starting aluminum and an infrared spectrum showed an Al—H stretching band at 1708 cm^{-1}.

Insoluble solid analysis. Found: Li/Al/H 3.12/1.00/6.10. Li_3AlH_6 calcd. Li/Al/H 3.00/1.00/6.00. An infrared spectrum (in nujol) gave a broad band centered at 1710 cm^{-1}. The X-ray powder diffraction pattern for this product is shown in Table 1.

Reaction of PhLi with $LiAlH_4$ in diethyl ether in 2/1 ratio

(a) In concentrated solution. When PhLi (7.85 mmol) in 7 ml of diethyl ether was allowed to react with 5 ml of a 7.8 *M* solution of $LiAlH_4$ in ether (3.9 mmol) at 0°C, a clear solution resulted. When this reaction mixture was stirred at room temperature for 1 h, a slight turbidity was observed which could not be separated by filtration. A infrared spectrum of this solution exhibited an Al—H stretching band at 1705 cm^{-1}. Analysis of this solution showed that it contained Li, Al, H and Ph in molar ratios 3.05/1.00/3.97/2.02.

When this reaction mixture was stirred further for 10 h, and more diethyl ether (20 ml) added, a white solid precipitated from the solution. Analysis of this solid showed that it contained Li, Al, H and Ph in ratios of 7.40/1.00/8.95/0.29. It gave no X-ray pattern.

(b) In dilute solution. When 5.00 mmol of $LiAlH_4$ in 15 ml of diethyl ether was added dropwise to a well-stirred solution of PhLi (10.0 mmol) in 20 ml of diethyl ether, an insoluble white precipitate formed. The reaction mixture was stirred for 1 h at room temperature and the insoluble solid was filtered, washed with diethyl ether and dried under vacuum. Analysis of the filtrate showed that it contained Li, Al, H and Ph in the ratio 1.07/1.00/1.97/2.05. An infrared spectrum of the filtrate showed a band at 1710 cm^{-1} due to Al—H stretching.

Insoluble solid analysis. Found: Li/Al/H/Ph 1.00/0.07/1.05/0.02 LiH calcd.: Li/Al/H/Ph 1.00/0.00/1.00/0.00. The X-ray powder diffraction pattern is reported in Table 1.

TABLE 1

X-RAY POWDER DIFFRACTION DATA (w, weak; m, medium; s, strong; v, very)

LiH[a]		Li_3AlH_6[b]		Li_3AlH_6[c]		LiH[d]		LiH[e]		LiH + $LiAlPh_4$[f]		$LiAlPh_4$[g]	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
3.85	w	4.06	vs	6.70	w	3.85	w	6.90	vw	8.50	s	8.51	s
2.65	w	3.96	vs	4.40	vs	2.80	w	4.80	vw	6.80	w	6.80	w
2.60	w	3.29	vvw	3.30	w	2.66	w	3.82	w	6.01	mw	6.00	m
2.35	s	3.18	vw	2.81	s	2.35	m	2.81	w	5.41	vw	5.41	vw
2.25	m	2.825	s	2.55	w	2.02	ms	2.76	w	4.80	vw	4.80	vw
2.03	s	2.555	m	2.32	s	1.43	m	2.65	w	4.40	vs	4.40	vs
1.95	w	2.500	w	2.25	w	1.22	w	2.33	m	4.11	s	4.15	s
1.59	w	2.340	vw	2.20	w	1.17	w	2.00	ms	3.80	w	3.80	w
1.440	s	2.318	vs	1.96	w	1.02	w	1.43	m	3.25	ms	3.25	ms
1.225	m	2.260	m	1.80	m			1.21	w	2.95	m	2.96	m
1.175	w	2.028	mw	1.76	m			1.16	w	2.13	vw	2.82	w
0.935	w	1.972	mw	1.52	m			1.02	w	2.05	vw	2.76	w
0.911	w	1.805	m	1.50	w			0.91	w	2.00	vw	2.63	w
		1.774	ms	1.47	w					1.90	w	2.55	w
		1.646	vw	1.41	vw					1.78	w	2.43	w
		1.530	ms	1.33	vw					1.58	w	2.30	vw
		1.507	m	1.31	vw							2.25	vw
		1.480	m	1.27	vw							2.13	vw
		1.411	w	1.25	vw							2.05	vw
		1.347	w	1.21	vw							2.00	vw
		1.333	w	1.15	vw							1.90	w
		1.316	w	1.10	vw							1.78	w
		1.277	w	1.08	vw							1.58	w
		1.250	w	1.04	vvw								
		1.218	w	1.03	vvw								
		1.158	w										
		1.122	w										
		1.115	w										
		1.102	w										
		1.088	w										

[a] Ref. 8. [b] Ref. 9. [c] PhLi + $LiAlH_4$. [d] 2 PhLi + $LiAlH_4$. [e] 3 PhLi + $LiAlH_4$. [f] 4 PhLi + $LiAlH_4$ → 4 LiH + $LiAlPh_4$.
[g] PhLi + Ph_3Al → $LiAlPh_4$.

Reaction of PhLi with $LiAlH_4$ in diethyl ether in 3/1 ratio

When 4.0 mmol of $LiAlH_4$ in 12 ml of diethyl ether was added dropwise to a well-stirred solution of PhLi (12.0 mmol) in 25 ml of diethyl ether, a precipitate appeared immediately. This reaction mixture was stirred at room temperature for 1 h and the solid was filtered, washed with diethyl ether and dried under vacuum. Analysis of the filtrate revealed that it contained Li, Al, H and Ph in ratios 1.00/1.00/0.95/3.06. An infrared spectrum of the filtrate exhibited a weak band at 1680 cm^{-1} due to Al—H stretching. Analysis of the solid showed it to contain Li, Al, H and Ph in molar ratios of 1.05/0.06/1.06/0.10. The X-ray powder diffraction pattern is given in Table 1.

Reaction of PhLi with $LiAlH_4$ in 4/1 ratio

To a well-stirred solution of PhLi (10.5 mmol) in diethyl ether was added dropwise a solution of $LiAlH_4$ (2.62 mmol) in diethyl ether. The reaction mixture was stirred at room temperature for 1 h to give an insoluble, highly viscous, pasty solid substance. The supernatant solution contained about 2—5% of the starting aluminum. Analysis of the supernatant solution revealed that it contained Li, Al, H and Ph in the molar ratio 1.06/1.00/0.01/4.10. Analysis of the insoluble pasty solid showed that it contained Li, Al, H and Ph in the molar ratio 5.08/1.00/3.95/4.05. (4 LiH + $LiAlPh_4$) calcd.: Li/Al/H/Ph 5.00/1.00/4.00/4.00. The insoluble pasty solid, when dried under vacuum, resulted in a white crystalline solid. This white solid was placed in THF and stirred for 15 minutes during which time most of the solid dissolved. Analysis of the white solid, insoluble in THF, showed it contained Li, Al, H and Ph in the molar ratio 1.02/0.02/1.00/0.03. The X-ray powder diffraction pattern is given in Table 1.

Reaction of CH_3Li with $LiAlH_4$

When 2.1 mmol of $LiAlH_4$ in 3 ml of diethyl ether was added dropwise to a well-stirred solution of methyllithium (5 ml, 4.2 mmol) in diethyl ether, precipitation occurred immediately. The precipitate did not redissolve even when the reaction mixture was stirred for 2 h. The insoluble white solid was filtered, washed with ether and dried in vacuo. The infrared spectrum of the filtrate showed an Al—H stretching band at 1708 cm^{-1} (characteristic of $LiAlH_2Me_2$). Analysis of the insoluble solid showed that it contained Li, Al, H in the ratio 1.00/0.11/1.14. LiH calcd.: Li/Al/H 1.00/0.00/1.00.

Preparation of $LiAlH_2Ph_2$

To a slurry of $LiAlPh_4$ (2.839 g; 8.30 mmol) in ether was added dropwise 20 ml of a 0.615 *M* solution of $LiAlH_4$ in diethyl ether (2.30 mmol) with constant stirring. This reaction mixture was stirred for 1 h after a clear solution was obtained. The diethyl ether was removed under vacuum, producing a pasty mass which crystallized after standing for 3 days at room temperature. Elemental analysis gave the following ratio: Li/Al/H/Ph/Et_2O 1.02/1.00/2.06/1.98/1.94. $LiAlH_2Ph_2 \cdot 2\ Et_2O$ calcd.: Li/Al/H/Ph/Et_2O 1.00/1.00/2.00/2.00/2.00. The infrared spectrum of this product in diethyl ether showed a strong band at 1709 cm^{-1} due to ν(Al—H) and the NMR spectrum showed two multiplets centered at 5.93 and 6.55 ppm downfield from the diethyl ether triplet. The internal chemical shift separation, δ_{int}, between the highest peaks of these two multiplets was observed to be 0.62 ppm.

Preparation of $LiAlHPh_3$

To a slurry of $LiAlPh_4$ (6.26 g; 12.45 mmol) in diethyl ether was added dropwise 10.0 ml of a 0.615 *M* solution (4.15 mmol) of $LiAlH_4$ in diethyl ether. The resulting solution was stirred for 1 h and excess solvent was removed under vacuum. When about 10 ml of ether remained, a white crystalline product appeared which was separated by decantation, washed with diethyl ether and dried at room temperature under reduced pressure (0.05 mmHg) for 15 min. The crystalline product then changed to a viscous mass. When freshly distilled diethyl ether was added to this viscous product, it again changed to a crystalline solid. The solid was separated and dried at 0°C for 1 h under vacuum (0.05 mmHg) and then analyzed. Elemental analysis gave the following ratio: $Li/Al/H/Ph/Et_2O$ 1.05/1.00/0.97/3.03/4.09. $LiAlHPh_3 \cdot 4\ Et_2O$ calcd.: $Li/Al/H/Ph/Et_2O$ 1.00/1.00/1.00/3.00/4.00. The infrared spectrum of the product in diethyl ether showed a band at 1680 cm^{-1} due to $\nu(Al—H)$.

Results and discussion

Ehrlich and coworkers [9] reported in 1966 that the reaction of $LiAlH_4$ with n-butyllithium in 1/2 molar ratio produced Li_3AlH_6 as an insoluble solid. It was

$$LiAlH_4 + 2\ n\text{-}C_4H_9Li \rightarrow Li_3AlH_6 + 2\ C_4H_8 \qquad (3)$$

proposed that the decomposition of n-butyllithium produced LiH and butene almost quantitatively [10], and the LiH so produced reacted with $LiAlH_4$ to form Li_3AlH_6. When we allowed PhLi and $LiAlH_4$ to react in diethyl ether in 1/1 molar ratio, an insoluble solid was obtained. This solid was characterized by elemental analysis, infrared and X-ray powder diffraction analysis to be Li_3AlH_6. The filtrate has been shown to contain $LiAlH_2Ph_2$ as characterized by elemental analysis and infrared spectroscopy (the reaction solution showed an Al—H stretching band at 1708 cm^{-1} characteristic of $LiAlH_2Ph_2$ [11]). An NMR spectrum of the filtrate also showed two multiplets centered at 5.93 and 6.55 ppm downfield from the diethyl ether triplet. The upfield multiplet was attributed to the *meta/para* protons of the phenyl group and the low field multiplet was attributed to the *ortho* protons of the phenyl group. The NMR spectrum was also identical to the spectrum obtained for an authentic sample of $LiAlH_2Ph_2$ (prepared by the redistribution of $LiAlH_4$ with $LiAlPh_4$). The probable reaction scheme is shown in eqs. 4 and 5.

$$2\ PhLi + LiAlH_4 \rightarrow 2\ LiH + LiAlH_2Ph_2 \qquad (4)$$

$$2\ LiH + LiAlH_4 \rightarrow Li_3AlH_6 \qquad (5)$$

This scheme is proposed on the basis that when $LiAlH_4$ was added to phenyllithium in 1/2 molar ratio, the only solid formed was lithium hydride. This reaction (eq. 6) was confirmed by the elemental and X-ray powder diffraction analy-

$$2\ PhLi + LiAlH_4 \rightarrow 2\ LiH + LiAlH_2Ph_2 \qquad (6)$$

sis of the insoluble solid (LiH) and by elemental analysis and an infrared spectrum comparison of the filtrate with an authentic sample of $LiAlH_2Ph_2$.

Interestingly, when the above reaction (eq. 6) was carried out in concentrated solution, a clear solution resulted. The infrared spectrum of this solution exhibited an Al—H stretching band at 1705 cm^{-1}. However, when the clear reaction mixture was diluted with diethyl ether, LiH precipitated. The LiH contained about 10% aluminum impurity. In concentrated solution an intermediate complex, $Li_3AlH_4Ph_2$, probably was formed which was soluble in diethyl ether and which on dilution dissociated with precipitation of LiH (eq. 7).

$$2\ PhLi + LiAlH_4 \rightarrow Li_3AlH_4Ph_2 \rightarrow 2\ LiH + LiAlH_2Ph_2 \qquad (7)$$

Since $LiAlH_4$ exhibits an Al—H stretching band at 1740 cm^{-1} in diethyl ether and the solution from the reaction of phenyllithium with $LiAlH_4$ in 2/1 molar ratio in concentrated solution showed an Al—H stretching band at 1705 cm^{-1}, the possibility of no reaction between 2 PhLi and $LiAlH_4$ in concentrated solution was overruled. Furthermore, $LiAlH_2Ph_2$ exhibits its Al—H band at 1710 cm^{-1} and the solution from reaction 6 carried out in concentrated form exhibited a band at 1705 cm^{-1}. Therefore, it seems that $Li_3AlH_4Ph_2$ probably is formed.

Because of the complex nature of the NMR spectra of compounds containing phenyl groups, it was decided that a methyl analog of $Li_3AlH_4Ph_2$, i.e. $Li_3AlH_4Me_2$ should be prepared in order to provide evidence for $Li_3AlH_4Ph_2$. An attempt was made to prepare $Li_3AlH_4Me_2$ by the reaction of $LiAlH_4$ with MeLi in diethyl ether in concentrated solution. When $LiAlH_4$ was added dropwise to a well-stirred solution of MeLi in diethyl ether, an immediate precipitation resulted which did not dissolve even after prolonged stirring. The insoluble solid was shown to be LiH contaminated with about 10% aluminum. The mode of addition of reagents did not effect the products.

In the reaction of phenyllithium with $LiAlH_4$ in 3/1 molar ratio, lithium hydride (as an insoluble solid) and $LiAlHPh_3$ (in solution) were formed. The solution containing $LiAlHPh_3$ showed an Al—H stretching band at 1680 cm^{-1} in the infrared spectrum [9] which was identical to the spectrum observed for the redistribution of $LiAlH_4$ and $LiAlPh_4$ in 1/3 ratio. An NMR spectrum of the filtrate

$$LiAlH_4 + 3\ LiAlPh_4 \rightarrow 4\ LiAlHPh_3 \qquad (8)$$

exhibited two multiplets almost at the same position where the multiplets of $LiAlHPh_3$ had been observed. However, the chemical shift separation between the two multiplets was 0.61 ppm, while in the case of $LiAlH_2Ph_2$ it was 0.62 ppm. Thus, the reaction proceeds as shown in eq. 9.

$$3\ PhLi + LiAlH_4 \rightarrow 3\ LiH + LiAlHPh_3 \qquad (9)$$

When $LiAlH_4$ was allowed to react with PhLi in 1/4 molar ratio, an insoluble pasty solid was formed. Analysis of the latter showed it to be a mixture of 4 LiH and $LiAlPh_4$ ($LiAlPh_4$ is insoluble in diethyl ether). When this solid was dried under vacuum, it crystallized. An X-ray diffraction pattern of this solid was similar to that of a sample of $LiAlPh_4$ prepared by the reaction of PhLi with Ph_3Al in diethyl ether. When the solid was treated with THF, most of the solid dissolved and the insoluble solid remaining was characterized as LiH. The reaction proceeds then as shown in eq. 10.

$$4\ PhLi + LiAlH_4 \rightarrow 4\ LiH + LiAlPh_4 \qquad (10)$$

The conclusion of these studies is that LiH is formed in the reaction of PhLi with $LiAlH_4$ in ether when the reaction is carried out in 4/1, 3/1 or 2/1 molar ratio, whereas Li_3AlH_6 is formed when the reaction is carried out in 1/1 molar ratio. Reaction of phenyllithium with $LiAlH_4$ in THF could not be carried out as phenyllithium cleaved THF very rapidly even at —15°C.

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