Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

PREPARATION AND CHARACTERIZATION OF LITHIUM- AND TETRAALKYLAMMONIUM TETRABUTYLALUMINATES

T. D. WESTMORELAND, JR., NASEER AHMAD* AND M. C. DAY**

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803 (U.S.A.)

(Received June 15th, 1970)

SUMMARY

Lithium tetra-n-butylaluminate ($LiAlBu_4$) has been prepared by reacting n-hexane solutions of n-butyllithium and tri-n-butylaluminum. The tetraalkylammonium tetra-n-butylaluminates (R_4NAlBu_4; R = Me, Et, n-Pr, n-Bu) have been prepared in benzene by the addition of sodium tetra-n-butylaluminate ($NaAlBu_4$) to solutions of R_4NBr. The significance of the syntheses of these salts for the study of ion–ion and ion–solvent interactions has been discussed.

The tetra-n-butylaluminate salts have been characterized by aluminum analyses, NMR spectroscopy, solubility data, melting points, and conductance data. The similarity between the physical and chemical properties of the R_4NAlBu_4 salts and $NaAlBu_4$, which has been extensively used for ion–solvent studies, indicates the potential value of these quaternary ammonium salts in analogous investigations.

INTRODUCTION

The unique ability of sodium tetra-n-butylaluminate ($NaAlBu_4$) to dissolve in solvents of low dielectric constant, including saturated hydrocarbons, has facilitated the study of specific ion-solvent interactions without interference from the bulk solvent[1]. A number of investigations utilizing this property of $NaAlBu_4$ have now been made on the specific complexation of the sodium ion by basic solvents[1-7]. Ideally, one would like to extend studies of this type to include the effect of cation size, but this would require a series of salts having a common anion with significant solubility in noncoordinating solvents.

Sodium tetra-n-butylaluminate has the distinct advantage of appreciable solubility in a variety of solvents, including those that can be considered essentially inert towards complexation. With the intent of conducting a study of the effects of cation size on both ion–solvent and ion–ion interactions, we have attempted to prepare a series of tetra-n-butylaluminate salts with the anticipation of solubility and ionic characteristics similar to those of the sodium salt.

We feel that the simple presentation of physical data and analyses is often in-

---

[*] On study leave from Aligarh Muslim University, Aligarh, India.

[**] To whom correspondence should be addressed.

adequate in the identification of certain chemical compounds, especially those which have been prepared for specific purposes. We have thus attempted to characterize the compounds which we have synthesized by presenting a cursory examination of experimental results, utilizing techniques which have been used in this laboratory for the study of $NaAlBu_4$.

The lithium salt, unfortunately, appears to be insoluble in non-polar solvents at ambient temperatures, and the potassium, cesium, and ammonium salts have never been successfully prepared in this laboratory. The preparation of the quaternary ammonium salts (R_4NAlBu_4), however, has been effected, and they are all appreciably soluble in benzene at room temperature. We wish to report here the preparative procedure for these salts, as well as that of lithium tetra-n-butylaluminate ($LiAlBu_4$), and to present their characterization.

RESULTS AND DISCUSSION

Proton magnetic resonance

The NMR spectra of aqueous solutions of the R_4NBr salts were recorded by a 60 MHz spectrometer, and the proton signals were analyzed. The proton resonance spectrum of $NaAlBu_4$ has previously been studied extensively in this laboratory[1], and a portion of the spectrum has been published by Wuepper and Popov[6]. The spectra which we recorded for the 0.1 *M* benzene solutions of the R_4NAlBu_4 salts were almost composite pictures of the spectra of the starting materials, $NaAlBu_4$ and R_4NBr. A 100 MHz spectrometer was used to obtain spectra of 250 Hz width to study the areas of the spectra in which overlap of the proton signals from the alkyl groups on the nitrogen and the aluminum occurs. Integration of the peaks gave no quantitative results because of the overlapping of the signals, but the constancy of the relative peak heights of the various alkyl groups in many different samples eliminates the possibility of a simple admixture of the two starting materials in the benzene solutions. Corroborative data confirm this.

The spectrum of $LiAlBu_4$ was taken in tetrahydrofuran (THF) because of this compound's limited solubility in benzene. The proton signals were very nearly identical to those of $NaAlBu_4$ in THF. No signals from n-butyllithium or tri-n-butylaluminum were detected.

Melting points and aluminum analyses

Table 1 lists the melting points which were obtained for the lithium and the quaternary ammonium salts. The melting points of $NaAlEt_4$ and $NaAlBu_4$ are included for purposes of comparison. It should be noted that the melting point for $NaAlBu_4$ is slightly higher than that reported in the literature[1,6]. The close agreement between the experimental and the theoretical percentages of the aluminum analysis and the refinement of the preparative procedure for the salt lead us to believe that our value is more nearly correct. The inclusion of the melting point of $NaAlBu_4$ is intended to show the proximity of its melting point to the melting points of the R_4NAlBu_4 salts. The much higher melting point of $NaAlEt_4$[8,9], as compared to that of $NaAlBu_4$, indicates that the forces of attraction in the crystalline state are more alike among the five tetra-n-butylaluminates than for the $NaAlBu_4$ and its tetraethyl analog. Moreover, the tetramethyl- and tetraethylammonium tetraethylaluminates, as re-

TABLE 1

MELTING POINTS AND ALUMINUM ANALYSES OF TETRAETHYL- AND TETRA-n-BUTYLALUMINATES

Salt	M.p. (°C)	% Al	
		Calcd.	Found
$NaAlEt_4$	ca. 125[8,9]	16.23	16.11, 16.18
$NaAlBu_4$	67–69	9.69	9.67
$LiAlBu_4$	181–183	10.3	10.1
Me_4NAlBu_4	68–70	8.19	8.11
Et_4NAlBu_4	74–76	6.99	7.10
Pr_4NAlBu_4	52–54	6.11	6.02
Bu_4NAlBu_4	49–50	5.42	5.41
Me_4NAlEt_4	162–165[10]	12.5	[a]
Et_4NAlEt_4	185–189[10]	9.86	[a]

[a] Analyses not given.

ported by Zakharkin *et al.*[10], show much higher melting points than any of the R_4NAlBu_4 salts. We are led to suspect that the presence of the tetra-n-butylaluminate anion in the crystal structure is at least partially responsible for the lower melting points of these salts and perhaps for their greater solubilities in solvents of low dielectric constant. Until definitive X-ray work is done on these salts, however, it would be premature to attempt to draw conclusions.

The aluminum analyses are also included in Table 1. The analyses were difficult to obtain because of the air-sensitivity of these compounds and the difficulty of removing the solvents; however, the results show good agreement with the theoretical values.

Carbon and hydrogen analyses were not made because of their unreliability for these air-sensitive compounds.

Solubility

An attempt was made to carry out a solubility study on these salts in solvents of interest with the intent of compiling a solubility chart for the compounds. However, the lithium salt is not soluble in saturated hydrocarbons and shows appreciable solubility in benzene only at elevated temperatures. The R_4NAlBu_4 salts form two phases in the presence of saturated hydrocarbons and dissolve in benzene so readily that only an estimate of their solubility in benzene could be made. The R_4NAlBu_4 salts are at least as soluble in benzene as $NaAlBu_4$ is in cyclohexane (ca. 3 *M*)[1]; however, at higher concentrations in benzene large globular particles can be seen on close inspection. The extent of this effect is dependent on the salt and the temperature. Further addition of benzene gives a clear solution. The quaternary ammonium salts are very soluble in THF but, surprisingly, must be heated in order to prepare even 0.1 *M* solutions.

Conductance

Table 2 lists the equivalent conductances of the salts in 0.1 *M* and 0.01 *M* solutions of benzene and THF. The cursory examination of the conductances of the salts is intended primarily to show the extent of their ionicity. Conductance studies

TABLE 2

SUMMARY OF EQUIVALENT CONDUCTANCES OF SOLUTIONS OF BENZENE AND TETRAHYDROFURAN

Salt	$\Lambda^a \times 10^2$ in benzene ($cm^2 \cdot equiv^{-1} \cdot ohm^{-1}$)		$\Lambda^a \times 10^2$ in THF ($cm^2 \cdot equiv^{-1} \cdot ohm^{-1}$)	
	0.1 *M*	0.01 *M*	0.1 *M*	0.01 *M*
$NaAlEt_4$	Insol.	Insol.	2400	1260
$NaAlBu_4$	1.8	0	2290	980
$LiAlBu_4$	Insol.	0	630	1560
Me_4NAlBu_4	5.3	0.8	0	1550
Et_4NAlBu_4	0	1.1	0	1650
Pr_4NAlBu_4	0	1.8	0	1560
Bu_4NAlBu_4	32	1.1	430	500

[a] Equivalent conductance.

of $NaAlBu_4$ in cyclohexane and THF indicate that the sodium salt exists as some sort of ionic species in these solvents. We had hoped simply to show the similarity between the conductances of the R_4NAlBu_4 salts and $NaAlBu_4$ in order to further characterize the salts and to illustrate the potential usefulness of the compounds as ionic species which are soluble in solvents of low dielectric constant. However, it is obvious upon inspection of the conductance data that not only is the ionicity of the quaternary ammonium salts clearly demonstrated, but some rather interesting behavior is shown.

Inspection of Table 2 reveals the relative magnitude of the equivalent conductances of the sodium and the lithium salts. In THF, the differences in equivalent conductances for these salts may be rationalized in terms of apparent differences in ion mobilities, but, obviously, the possibility of ion pairs and higher aggregates must also be considered. It is particularly interesting to note the increase in equivalent conductance with an increase in salt concentration for the sodium salts in THF; whereas, the reverse is observed for the lithium and the R_4NAlBu_4 salts in this solvent.

The equivalent conductances of the R_4NAlBu_4 salts cannot be readily rationalized. In terms of previous conductance studies on similar salts, we might attribute the low equivalent conductances to large degrees of association[11-16]. Table 2 shows that the quaternary ammonium salts in benzene have essentially the same conductances at the lower concentrations. It is apparent that the ion size plays an extremely important role in these sytems; a role that is now under study in this laboratory.

Reactivity

The R_4NAlBu_4 salts are unstable in the presence of air, water, oxygen, and alcohols, as has been observed with the corresponding sodium salt; however, they appear to be much less reactive in these systems than $NaAlBu_4$. $LiAlBu_4$ is more reactive than $NaAlBu_4$. All of the compounds appear to be quite stable in the hydrocarbons and ethers we have used in our investigations.

EXPERIMENTAL

Conductance

Conductance cells of standard design with shiny platinum electrodes were used for all of the conductance measurements. The cells were fitted with outer ground-glass caps in order to prevent contamination of the solutions by the joint lubricant. The cell constants were determined by the use of potassium chloride solutions accordding to method of Lind *et al.*[17].

Conductance measurements were made by a Leeds and Northrup Model 4666 Jones Modified Conductance Bridge or by a RC-16 Conductance Bridge manufactured by Industrial Instruments, Inc. A Hewlett–Packard Model 200 D audio oscillator and a General Radio Company Type 1232 A tuned amplifier and null detector were used in conjunction with the Leeds and Northrup instrument. The oscillator was operated at 3000 Hz and had an output to the bridge of 0.5 V. The maximum resistance measurable on the RC-16 Conductance Bridge is 2.5 MΩ; that on the Jones Bridge is 60 kΩ. Measured resistances were taken with the Jones Bridge whenever possible. The temperature of the solutions were maintained at $30 \pm 1°$.

The conductance cells were thoroughly washed in acetone, ethanol, water, 20% HCl solution, 50% H_2SO_4 solution, and conductivity water before they were dried in an oven at 120° for several hours. The cells were taken directly from the oven and placed under vacuum in the port to the nitrogen-atmosphere dry box while they cooled. The conductance cells, as well as all other equipment and chemicals taken into the dry box, were kept in the port while the nitrogen atmosphere in the port was recirculated through a series of columns and traps to remove any traces of oxygen and moisture[2].

Conductances were not observed for the purified solvents; consequently, no corrections for solvent conductance were necessary. Conductance values for the solutions did not vary significantly over a 24 h period.

Proton magnetic resonance

The proton magnetic resonance spectra were taken for all compounds on the Varian Associates A-60A and HA-100 spectrometers at ~37°. NMR tubes were filled in the dry box and sealed with high pressure caps. Samples were run within approximately two hours of the time the tubes were removed from the dry box.

Solvents and reagents

All solvents were purchased as reagent grade chemicals. They were allowed to stand over CaH_2 until no further reaction was visible, refluxed over the CaH_2 for a minimum of 8 h, and distilled under an atmosphere of dry nitrogen gas. A portion of each solvent was poured over small amounts of the sodium and lithium salts of tetra-n-butylaluminate to test for traces of water and oxygen before the solvent was used. The THF was used within a period of 48 h from the time it was taken into the dry box.

The preparation and purification of $NaAlBu_4$ and $NaAlEt_4$ have been discussed in previous publications[1,8,9]. The R_4NBr salts were purchased as highest purity salts (Eastman Organic and J. T. Baker). They were subjected to a vacuum for several hours before use. Recrystallization was not deemed necessary for the use of the salts in the preparatory procedures.

The n-butyllithium (Alfa Inorganics) was used as a 22% hexane solution, and was filtered through glass wool in the dry box before use.

The tri-n-butylaluminum (Texas Alkyls) was used as a 95.9% pure reagent (highest purity) without further purification.

Preparation of $LiAlBu_4$

The procedure for the preparation of $LiAlBu_4$ is similar to that of Hurd's[18] preparation of $LiAlMe_4$. An equimolar ratio of tri-n-butylaluminum in hexane was added to n-butyllithium (22% hexane solution) in an inert atmosphere. The white crystals which formed immediately upon the mixing of the two solutions were filtered and washed with hexane four times. Recrystallization was effected in hot toluene. Washing with hexane, followed by the application of a vacuum to the crystals as they were rotated in a flask connected to a high vacuum rotating evaporator, gave fluffy white crystals.

Preparation of the R_4NAlBu_4 salts

All of the R_4NAlBu_4 salts were prepared by the same general procedure of refluxing a given quantity of the appropriate R_4NBr salt in benzene under a nitrogen atmosphere for 24–48 h in order to attain maximum solubility of the salt before adding a benzene solution of $NaAlBu_4$ dropwise to the refluxing mixture. A slight molar excess of the R_4NBr was used. The admixture was refluxed further for approximately 24 h. The NaBr and excess R_4NBr were removed by filtration in the dry box. The resultant solution was subjected to a vacuum until a viscous solution was obtained; whereupon, the solution was filtered again. The filtrate was washed with hexane several times to extract any excess $NaAlBu_4$ and then placed under vacuum in a high vacuum rotating evaporator until a thick slurry was obtained. Filtration of the slurry gave white crystals. After being washed with hexane, the crystals were heated to ~ 100° while being subjected to a vacuum to remove the last fraction of benzene and hexane.

Recrystallization was never adequately effected because of the large degree of solubility of the salts in benzene and their unusual property of forming two phases in the presence of hexane. Hence, the above procedure was repeated until a two degree (or less) melting point range was obtained for each salt. Both THF and diethyl ether were used as the carrying solvent in the initial studies, but the difficulty of the complete removal of the ethers caused us to rely on benzene.

The possibility of synthesizing R_4NAlR_4 compounds was reported by Lehmkuhl[19], although no preparative procedure was offered.

Aluminum analysis

The aluminum analyses were carried out on these salts according to a slight modification of the procedure outlined by Kolthoff and Sandell[20]. An average value of two or more analyses was reported for each salt.

ACKNOWLEDGEMENTS

Support of this work by National Science Foundation Grant Gp6421 is gratefully acknowledged. We also extend our gratitude to Dr. N. S. Bhacca for his consultation in the analysis of the NMR spectra.

REFERENCES

1 E. Schaschel and M. C. Day, *J. Amer. Chem. Soc.*, 90 (1968) 503.
2 C. N. Hammonds and M. C. Day, *J. Phys. Chem.*, 73 (1969) 1151.
3 E. G. Höhn, J. A. Olander and M. C. Day, *J. Phys. Chem.*, 73 (1969) 3880.
4 C. N. Hammonds, T. D. Westmoreland and M. C. Day, *J. Phys. Chem.*, 73 (1969) 4374.
5 A. T. Tsatsas and W. M. Risen, Jr., *J. Amer. Chem. Soc.*, 92 (1970) 1789.
6 J. L. Wuepper and A. I. Popov, *J. Amer. Chem. Soc.*, 92 (1970) 1493.
7 J. A. Olander and M. C. Day, to be submitted for publication.
8 E. B. Baker and H. H. Sisler, *J. Amer. Chem. Soc.*, 75 (1953) 5193.
9 F. W. Frey and P. Kobetz, *J. Org. Chem.*, 26 (1961) 2950.
10 V. V. Gavrilenko, Yu. N. Karaksin and L. I. Zakharkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1969) 1380; *Chem. Abstr.*, 71 (1969) 76855.
11 L. E. Strong and C. A. Kraus, *J. Amer. Chem. Soc.*, 72 (1950) 166.
12 J. Barthel, *Angew. Chem.*, 7 (1968) 260.
13 D. F. Evans, C. Zawoyski and R. L. Kay, *J. Phys. Chem.*, 69 (1965) 3878.
14 R. L. Kay, C. Zawoyski and D. F. Evans, *J. Phys. Chem.*, 69 (1965) 4208.
15 D. F. Evans and R. L. Kay, *J. Phys. Chem.*, 70 (1966) 366.
16 R. L. Kay and D. F. Evans, *J. Phys. Chem.*, 70 (1966) 2325.
17 J. E. Lind, J. J. Zwolenik and R. M. Fuoss, *J. Amer. Chem. Soc.*, 81 (1959) 1557.
18 D. T. Hurd, *J. Org. Chem.*, 13 (1948) 711.
19 H. Lehmkuhl, *Angew. Chem.*, 75 (1963) 1090.
20 I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, Macmillan, New York, 3rd ed., 1952, p. 320.