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Preparation of New Complex Metal Hydrides. Potassium Tetrahydrozincate and Sodium Tetrahydrozincate

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Potassium tetrahydrozincate (K_2ZnH_4) was prepared by the reaction of KH and di-*sec*-butylzinc in benzene and tetrahydrofuran and by the hydrogenation of $KZn(sec\text{-}C_4H_9)_3$ in tetrahydrofuran. The compound K_2ZnH_4 was characterized by X-ray powder diffraction, infrared spectroscopy, elemental analysis, and dta–tga. Evidence for the existence of Na_2ZnH_4 is also presented.

Introduction

In view of our recent report[1] of the preparation of $KMgH_3$ by the hydrogenation of $KMg(sec\text{-}C_4H_9)_2H$, we wished to expand the study to include other group II metals.

Our plan was to study the reaction of KH, NaH, and LiH with a dialkylzinc compound in both hydrocarbon and ether solvent in an attempt to prepare a number of alkali metal dialkylzinc hydrides in much the same way we have prepared similar magnesium compounds. The reactions were to be carried out using di-*sec*-butylzinc, since this compound is soluble in both hydrocarbons and ethers and the $sec\text{-}C_4H_9Zn$ group should be easily hydrogenolyzed to the HZn group

$$\begin{tikzcd}
 & \mathit{MZnH_3} + 2RH & \mathit{M_2ZnH_4} + 2RH & \mathit{M_3ZnH_5} + 2RH & \\
MH + R_2Zn \arrow[r] & MZnR_2H \arrow[u, "H_2"] \arrow[r, "MH"] \arrow[dr, "R_2Zn"'] & M_2ZnR_2H_2 \arrow[u, "H_2"] \arrow[r, "MH"] & M_3ZnR_2H_3 \arrow[u, "H_2"] & (1) \\
 & & MZn_2R_4H \arrow[r, "H_2"] & \mathit{MZn_2H_5} &
\end{tikzcd}$$

where M = Li, Na, K and R = $sec\text{-}C_4H_9$. The italic hydrides represent new complex metal hydrides of zinc.

Shriver and coworkers have recently reported the preparation of $MZnR_2H$ compounds in ether solvent[2] and have demonstrated the existence of MZn_2R_4H compounds in solution as well (eq 2).[2] Since new complex

$$MZnR_2H + ZnR_2 \rightleftarrows MZn_2R_4H \tag{2}$$

metal hydrides are of considerable interest both from a structural viewpoint and as selective reducing agents in organic chemistry, we wished to synthesize the new complex metal hydrides of zinc described above.

Experimental Section

Apparatus.—Reactions were performed under nitrogen at the bench. Filtrations and other manipulations were carried out in a glove box equipped with a circulating system using manganese oxide columns to remove oxygen and Dry Ice–acetone to remove solvent.[3]

Infrared spectra were obtained on a Perkin-Elmer 621 spectrophotometer as Nujol mulls between CsI plates. X-Ray powder data were obtained on a Philips Norelco X-ray unit using a 114.6-mm camera with nickel-filtered Cu Kα radiation. Samples were sealed in 0.5-mm capillaries and exposed to X-rays for 6 hr. *d* spacings were read on a precalibrated scale equipped with a viewing apparatus. Intensities were estimated visually. A 300-ml Magne-Drive autoclave (Autoclave Engineers, Inc.) was used for high-pressure hydrogenation. Dta–tga data were obtained at atmospheric pressure under argon on a Mettler Thermoanalyzer 2. Alumina crucibles were used to hold the samples.

Analyses.—Gas analyses were carried out by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[3] Alkali metals were determined by flame photometry. Zinc was determined by EDTA titration.

Materials.—Potassium and sodium hydrides were obtained from Alfa Inorganics as a slurry in mineral oil. A solution of lithium aluminum hydride (Ventron, Metal Hydride Division) was prepared in diethyl ether in the usual manner.

Diethyl- and di-*sec*-butylzinc were prepared by the Noller procedure.[4] Ethyl and *sec*-butyl iodides were obtained from Fisher Scientific. The iodides were dried over anhydrous $MgSO_4$ and distilled prior to use. The zinc–copper couple was obtained from Alfa Inorganics. The reactions were allowed to proceed overnight. The dialkylzinc was distilled from the reaction pot at reduced pressure. Analysis of the di-*sec*-butylzinc gave a butane to zinc ratio of 2.13:1.00.

Reaction of KH and $(sec\text{-}C_4H_9)_2Zn$ in Benzene.—Di-*sec*-butylzinc was added to a slurry of KH (34.4 mmol) in benzene previously washed with benzene to remove the mineral oil. The slurry became warm immediately and developed a slightly yellow color. A solid was always present during the reaction. The mixture was stirred overnight at room temperature. The solid was separated by filtration and dried at room temperature *in vacuo*. The resulting white solid was extremely reactive, flaming on exposure to the atmosphere. *Anal.* Calcd for K_2ZnH_4: K, 53.0; Zn, 44.3; H, 2.73. Found: K, 45.9; Zn, 37.4; H, 2.23. The molar ratio of K:Zn:H is 2.04:1.00:3.86. The amount of K_2ZnH_4 recovered was 5.5 mmol of an expected 8.6 mmol. The X-ray powder diffraction data are given in Table I. Infrared spectrum (Nujol mull) showed two strong broad bands at 500–800 cm^{-1} centered at 650 cm^{-1} and 1200–1600 cm^{-1} centered at 1400 cm^{-1}. Dta–tga showed that the sample still contained a little solvent which was lost below 80°. Thermal decomposition of the compound occurred endothermically at 242, 292, and 336°. The simultaneous weight loss curve showed inflections that corresponded to the loss of weight equivalent to one hydrogen each at the first two endotherms and to two hydrogens at the final endotherm. Analysis of the filtrate gave a ratio of K:Zn:H:C_4H_9 of 1.18:1.00:0.14:2.98. The filtrate contained 17 mmol of $KZn(sec\text{-}C_4H_9)_3$ based on zinc analysis.

Reaction of Excess KH with $(sec\text{-}C_4H_9)_2Zn$ in Tetrahydrofuran.—Di-*sec*-butylzinc (26.2 mmol) was added to a slurry of KH (59.3 mmol) in tetrahydrofuran. The KH had been previously washed with tetrahydrofuran to remove the mineral oil. The slurry became warm immediately turning slightly yellow. The mixture was stirred overnight. A solid remained throughout the

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(1) E. C. Ashby, R. Kovar, and R. Arnott, *J. Amer. Chem. Soc.*, **92**, 2182 (1970).

(2) G. J. Kubas and D. F. Shriver, *ibid.*, **92**, 1949 (1970).

(3) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

(4) C. R. Noller, *Org. Syn.*, **12**, 86 (1932).

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR K_2ZnH_4

K_2ZnH_4[a]		K_2ZnH_4 + Zn[b]		Zn[c]		K_2ZnH_4 + KH[d]		KH[e]		ZnH_2[f]	
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
5.10	w	5.10	w			5.05	w			4.51	vw
4.26	m	4.27	m			4.25	m			4.23	s
3.89	w	3.89	w			3.90	w			3.80	vw
3.62	vw	3.62	vw			3.60	vw			3.40	m
3.47	m	3.47	m			3.30	s	3.30	vs	2.97	vw
3.24	w	3.24	w			3.10	s			2.828	vw
3.09	s	3.08	s			2.95	s			2.608	w
2.940	s	2.941	s			2.85	s	2.86	s	2.468	vw
2.744	w	2.743	w			2.91	w			2.387	m
2.568	vvw	2.568	w			2.33	m			2.290	m
2.354	w	2.469	s	2.473	m	2.13	m			2.225	m
2.128	w	2.353	w			2.03	m	2.02	s	2.135	w
1.946	w	2.305	s	2.308	m	1.96	vw			2.085	w
1.814	w	2.128	w			1.82	vw			2.017	vw
1.734	w	2.090	vs	2.091	s	1.72	m	1.72	s	1.905	w
1.648	vw	1.945	w			1.64	w	1.65	m	1.764	w
1.624	vw	1.814	w			1.55	w			1.688	vw
1.571	w	1.734	w			1.49	vw	1.43	m	1.630	vw
1.488	w	1.681	s	1.687	m	1.39	vw	1.31	m	1.562	vw
1.470	w	1.648	vw					1.28	m	1.486	vw
1.384	vw	1.624	vw					1.17	m	1.464	vw
1.213	w	1.571	w					1.10	m	1.416	vw
		1.551	vw					1.01	w	1.336	vw
		1.487	w							1.305	vw
		1.471	vw							1.295	vw
		1.384	vw							1.259	vw
		1.340	s	1.342	m					1.219	vw
		1.330	s	1.332	m					1.172	vw
		1.236	w	1.237	w					1.157	vw
		1.213	w							1.123	vw
		1.172	w	1.173	m					1.042	vw
		1.153	s	1.154	w						
		1.123	w	1.124	w						
		1.090	m	1.091	w						
				1.046	w						

[a] KH + (*sec*-C_4H_9)$_2$Zn in benzene. [b] Hydrogenation of KZn(*sec*-C_4H_9)$_3$. [c] ASTM file. [d] Excess KH + (*sec*-C_4H_9)$_2$Zn. [e] ASTM files. [f] $LiAlH_4$ + $(C_2H_5)_2Zn$.

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR Na_2ZnH_4

Na_2ZnH_4 + Zn[a]		Zn[b]		K_2ZnH_4[c]	
d, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0
5.082	m			5.10	w
4.80	vw			4.26	m
4.04	m				
3.92	m			3.89	w
3.36	m			3.62	vw
3.07	w			3.47	m
2.921	w			3.24	w
2.751	s			3.09	s
2.585	w			2.940	s
2.468	s	2.473	m	2.744	w
2.373	m			2.568	vvw
2.306	s	2.308	m	2.354	w
2.156	w			2.128	w
2.087	vs	2.091	s		
1.964	vw			1.946	w
1.941	vw				
1.812	vw			1.814	w
1.749	vw				
1.683	s	1.687	m	1.734	w
1.644	vw			1.648	vw
1.596	vw			1.624	vw
1.553	vw			1.571	w
1.478	vw				
1.378	vvw			1.488	w
1.339	s	1.342	m	1.470	w
1.330	s	1.332	m	1.384	vw
1.236	vw	1.237	w	1.213	w
1.172	s	1.173	m		
1.149	w	1.154	w		
1.123	s	1.124	m		
		1.090	w		
		1.046	w		

[a] Hydrogenation of NaH[(*sec*-C_4H_9)$_2$Zn]$_2$. [b] ASTM files. [c] KH(*sec*-C_4H_9)$_2$Zn.

reaction. The solid was separated by filtration and dried *in vacuo* at room temperature. Analysis showed a ratio of K:Zn:H of 3.23:1.00:4.68. X-Ray powder data are given in Table I.

Analysis of the filtrate showed a ratio of K:Zn:H:*sec*-C_4H_9 of 0.96:1.00:0.26:2.87. The filtrate was subjected to hydrogenation at 3000 psi and 40° for 24 hr. A black precipitate was recovered from the autoclave. X-Ray powder pattern is shown in Table I.

Reaction of NaH and (*sec*-C_4H_9)$_2$Zn in Benzene.—Di-*sec*-butylzinc (31.9 mmol) was added to a slurry of NaH (42.6 mmol) in benzene. The NaH had been previously washed with benzene to remove the mineral oil. No immediate reaction was obvious. After stirring 1 week, analysis of the supernatant showed a Zn:*sec*-C_4H_9 ratio of 1:2.09 with no hydridic hydrogen.

Reaction of NaH and (*sec*-C_4H_9)$_2$Zn in Dimethoxyethane.—Di-*sec*-butylzinc (16.7 mmol) was added to a slurry of NaH (excess) in dimethoxyethane. Analysis of the supernatant after stirring for 1 week showed a zinc:hydride ratio of 2:1. The mixture was filtered and the filtrate subjected to hydrogenation at 3000 psig and 40° for 2 hr. A black precipitate was isolated from the autoclave. X-ray powder diffraction pattern is shown in Table II. Dta-tga spectrum of the precipitate showed weak endotherms at 190, 220, and 265° with a corresponding continuous weight loss and a strong endotherm at 322° with no weight loss.

Attempt to Prepare ZnH_2 by Hydrogenation of (*sec*-C_4H_9)$_2$Zn in Benzene.—A benzene (100 ml) solution of (*sec*-C_4H_9)$_2$Zn (35.4 mmol) was hydrogenated overnight at 3000 psi at room temperature. No reaction occurred. The hydrogenation was repeated at 50°. A black precipitate resulted which was shown to be elemental zinc by X-ray powder diffraction.

Preparation of ZnH_2 by $LiAlH_4$ Reduction of (*sec*-C_4H_9)$_2$Zn.—Lithium aluminum hydride (14.1 mmol) in diethyl ether (30 ml) was slowly added to diethylzinc (9.4 mmol) in diethyl ether (25 ml). The reaction was allowed to stir overnight at room temperature and the precipitate isolated by filtration. *Anal.* Calcd for ZnH_2: Zn, 97.0; H, 2.99. Found: Zn, 87.2, H, 2.69. The X-ray powder pattern is shown in Table I. Dta-tga spectrum of ZnH_2 showed a very rapid exothermic *decomposition at 85°*.[5]

Results and Discussion

Contrary to the reaction of dialkylzinc compounds with NaH and LiH to form R_2Zn–MH complexes in ether solvents,[2] KH and di-*sec*-butylzinc were found to react directly to form a new hydride, K_2ZnH_4, both in hydrocarbon and ether solvent

$$4KH + 3R_2Zn \longrightarrow K_2ZnH_4 + 2KZnR_3 \quad (R = sec\text{-}C_4H_9) \quad (3)$$

The reaction is relatively rapid and the isolation of an intermediate R_2Zn–KH complex was not possible. The X-ray powder pattern of K_2ZnH_4 contained no lines for KH or ZnH_2 (Table I). When a reaction with excess KH was carried out, the X-ray powder diffraction pattern showed lines for KH in addition to the lines for K_2ZnH_4 (Table I). Zinc hydride was prepared by the reaction of $LiAlH_4$ and $(C_2H_5)_2Zn$ in diethyl ether after an attempt to prepare it by the hydrogenation of (*sec*-C_4H_9)$_2$Zn failed. The X-ray powder pattern of ZnH_2 is included in Table I.

Since no complex of KH and dialkylzinc could be isolated for hydrogenation, an attempt was made to prepare $KZnH_3$ by the hydrogenation of KZn(*sec*-C_4H_9)$_3$ in tetrahydrofuran. The hydrogenation (eq 4) produced a black precipitate which was shown by X-ray powder pattern to be a mixture of K_2ZnH_4 and elemental zinc (Table I). Apparently K_2ZnH_4 is the most stable complex potassium zinc hydride.

$$2KZn(sec\text{-}C_4H_9)_3 + 3H_2 \longrightarrow K_2ZnH_4 + Zn + 6C_4H_{10} \quad (4)$$

In contrast to ZnH_2 which decomposes slowly at room temperature and rapidly at 85°, K_2ZnH_4 is very ther-

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mally stable. Dta–tga analysis shows endotherms during decomposition at 242, 292, and 336°.

The infrared spectrum (Nujol mull) of K_2ZnH_4 shows two strong broad bands at 1400 and 650 cm^{-1}. These bands are consistent with octahedral coordinated zinc, since in the related system of magnesium hydrides (MgH_2 and $KMgH_3$) where the magnesium is known to be octahedrally coordinated, broad infrared bands occur at 1160 and 650 cm^{-1}.[6]

Although we have not indexed the powder pattern, the most likely structure of K_2ZnH_4 would seem to be that of K_2ZnF_4[7] which is the K_2NiF_4[8] structure.

We observed that NaH and di-*sec*-butylzinc do not react in hydrocarbon; however a 1:2 complex of NaH:(*sec*-$C_4H_9)_2Zn$ [$NaZn_2R_4H$] was formed in dimethoxyethane. Although NaH was used in excess, a 1:1 ($NaZnR_2H$) or 2:1 ($Na_2ZnR_2H_2$) complex was not observed. Hydrogenation of this complex produced a black solid. The X-ray powder diffraction pattern (Table II) indicated that the solid was a mixture of zinc metal and another compound with a similar pattern to K_2ZnH_4, probably Na_2ZnH_4. When the black solid was subjected to dta–tga, a decomposition pattern similar to that observed for K_2ZnH_4 was obtained. The stepwise endothermic decomposition occurs at slightly lower temperatures: 190, 220, and 265°. A fourth endotherm is observed at 322° with no weight loss that is associated with the melting of zinc metal. On the basis of the X-ray powder pattern and the dta–tga, the existence of Na_2ZnH_4 seems likely.

An attempt to prepare $LiZnH_3$ or Li_2ZnH_4 by hydrogenolysis of the reaction production of *sec*-C_4H_9Li and (*sec*-$C_4H_9)_2Zn$ in benzene solvent was not successful. Instead, a solid product was produced which exhibited an X-ray powder pattern characteristic of LiH. It was hoped that reaction of Li-*sec*-C_4H_9 and Zn(*sec*-$C_4H_9)_2$ would take place to produce LiZn(*sec*-$C_4H_9)_3$ which then would be hydrogenalyzed to form either $LiZnH_3$ or Li_2ZnH_4

$$\text{Li-}sec\text{-}C_4H_9 + (sec\text{-}C_4H_9)_2Zn \longrightarrow LiZn(sec\text{-}C_4H_9)_3 \overset{H_2}{\not\longrightarrow} LiZnH_3 \text{ or } Li_2ZnH_4 \quad (5)$$

Work is in progress to prepare other complex metal hydrides of zinc.

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High-Silica Analogs of Zeolite A Containing Intercalated Phosphate

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Extension of the phosphate-complexing technique to the mixed tetramethylammonium–sodium system led to the crystallization of high-silica zeolites of type A structure as well as a high-silica sodalite. The products of zeolite A crystal structure were found to contain intercalated phosphate, in amounts up to 1 phosphorus per sodalite cage, whereas the high-silica sodalite did not contain phosphorus. Two types of zeolites of the same crystal structure were distinguished: one type, classified as zeolite ZK-21, crystallized in the sodium form; the other, zeolite ZK-22, had an exchangeable cation to aluminum ratio of less than 1 because of the presence of nonexchangeable tetramethylammonium ions trapped during crystallization. As all materials of zeolite A structure, these two zeolites sorb straight-chain hydrocarbons if the number of cations per unit cell is not greater than 10. The more siliceous of the ZK-21's and ZK-22's, in their lanthanum and hydrogen forms, are stable, shape-selective cracking catalysts with an interconnected three-directional channel network.

The use of phosphate as a complexing agent for aluminate in the preparation of zeolite Y has been reported previously.[1] The study disclosed that the equilibrium

$$Al(PO_4)_2^{3-} + 4OH^- \rightleftarrows Al(OH)_4^- + 2PO_4^{3-}$$

is responsible for the increase in the silica to alumina ratio of the product when phosphate is present in the reaction mixture. The complex was identified as a diphosphatoaluminate.[2]

The phosphate-complexing technique yielded a variety of high-silica zeolites with faujasite,[1] chabazite,[1] and phillipsite structures.[1,3] It has also been applied successfully to the gallosilicate system,[1,4] yielding a high-silica gallosilicate zeolite of faujasite structure.

So far, only sodium and potassium had been used as cations in mixtures containing phosphate. When a combination of sodium and tetramethylammonium was used, high-silica, phosphate-containing zeolites of type A structure were obtained. (For a detailed description of zeolite structures see ref 5.) Preparations and properties of these materials are described in this paper.

A zeolite of type A structure containing organo-substituted ammonium ions was first synthesized by Barrer and Denny.[6] The yield was low, and a complete

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