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## Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

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Published online: 22 Aug 2006.

To cite this article: Wenming Zhang , Shijian Liao , Yun Xu & Yiping Zhang (1997) Application of Alkali Metal Hydrides of Nanometric Size in Reduction, Cyclotrimerization and Metalation, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 27:22, 3977-3983

To link to this article: http://dx.doi.org/10.1080/00397919708005919

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### APPLICATION OF ALKALI METAL HYDRIDES OF NANOMETRIC SIZE IN REDUCTION, CYCLOTRIMERIZATION AND METALATION

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Abstract: Reactions of some representative organic functional compounds by the alkali metal hydrides of nanometric size have been studied. Nitrobenzene, some aldehydes, esters and organic halides are reduced with good yield and high selectivity in many cases. Nitriles are cyclotrimerized and dimethyl sulfoxide is rapidly deprotonated.

Commercial alkali metal hydrides have been widely used in organic synthesis. However, for many reactions, the activity of these hydrides should be improved<sup>1-4</sup>. A great deal of effort has been devoted to activate the commercial hydrides<sup>5-8</sup> or to prepare highly reactive form of alkali metal hydrides by new methods, such as hydrogenolysis of organometallic compounds<sup>9,10</sup>, or in the presence of TMEDA (tetramethylethylenediamine)<sup>11</sup>.

Alkali metal hydrides of nanometric size LiH<sup>\*</sup>, NaH<sup>\*</sup> and KH<sup>\*</sup> have been prepared catalytically by the direct hydrogenation of alkali metals under atmospheric pressure<sup>12-15</sup>. Transmission electron micrographs show that the average primary particle sizes of KH<sup>\*</sup>, NaH<sup>\*</sup> and LiH<sup>\*</sup> are 19, 23 and 22 nm, respectively, in contrast to the commercial NaH of ~2.5µm (from Serva, Germany). The specific surface area of NaH<sup>\*</sup> and KH<sup>\*</sup> are 90 and 50 m<sup>2</sup>/g,

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respectively, as calculated from BET measurements<sup>15</sup>. Due to their very small primary particle sizes and large specific surface areas, these alkali metal hydrides can be classified into the category of the nanomaterials, in which the surface species play a very important role. Consequently, they display very different behaviors from those of the commercial materials. In this paper we report the reactions of some representative organic compounds with these highly reactive forms of alkali metal hydrides of nanometric size.

#### 1. REDUCTIONS:

Table 1 reports the reductions of some representative organic functional groups with various metal hydrides. In the reduction of aromatic carbonyl compounds, commercial NaH reduces benzaldehyde to benzyl alcohol in 12% yield after 4h and methyl benzoate to benzaldehyde in 0.1% yield after 15h. Under the same reaction conditions, all of these highly reactive hydrides MH\* reduce benzaldehyde completely in 4h. It appears that the reductions of methyl benzoate with NaH\* and LiH\* give much lower conversions and selectivities than that with KH\*. However, when an equal molar ratio of Ni(OAc)<sub>2</sub> to the substrate is added to NaH\*, methyl benzoate can be reduced with high conversion and selectivity in 4h under the same conditions.

When KH\* is used in the reduction of terephthalaldehyde, the substrate converts completely in 1h, but the reduction of the intermediate product p-(CHO)C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>OK) is much slower. Thus, the selective reductions of one aldehyde group in the analogues of terephthalaldehyde may be achieved under suitable reaction conditions.

The essential results of reductions of acrolein and acrylates show that NaH\* reduces acrolein to allyl alcohol in 97% yield in 18 min, and it rapidly converts methyl and *n*-butyl acrylates to the only product allyl alcohol with excellent conversion and high selectivity ( without the intermediate, acrolein, and the C=C bond remains unchanged). Apparently, methyl ester reacts much faster than *n*-butyl ester, and such rate difference should be due to the larger steric hindrance of *n*-butyl group.

Nitrobenzene can be reduced by NaH\* to azoxybenzene as the main product, but commercial NaH gives much lower yield

The commercial NaH itself is a poor reducing agent for the hydrogenolysis of organic halides. For example, it is inert to 1-bromonaphthalene in refluxing THF

Substrate	MH	R <sup>a</sup>	Time	Product	
			(h)	(yield, %)	
Benzaldehyde	NaH <sup>b</sup>	1.8	4	Benzyl alcohol(12)	
Benzaldehyde	LiH*	1.8	4	Benzyl alcohol(100)	
Benzaldehyde	NaH*	1.8	4	Benzyl alcohol(100)	
Benzaldehyde	KH*	1.8	4	Benzyl alcohol(100)	
Methyl benzoate	NaH <sup>b</sup>	3.6	15	Benzaldehyde(0.1)	
Methyl benzoate	LiH*	3.6	15	Benzaldehyde(5) benzyl alcohol(25)	
Methyl benzoate	NaH*	3.6	15	Benzaldehyde(18) benzyl alcohol(26)	
Methyl benzoate	NaH* <sup>c</sup>	3.6	15	Benzaldehyde(8) benzyl alcohol(92)	
Methyl benzoate	KH*	3.6	15	Benzaldehyde(6) benzyl alcohol(94)	
Terephthalaldehyde	KH*	3.6	1	4-Formyl benzyl alcohol(62.5)	
				1,4-Benzenedimethanol(36.5)	
Terephthalaldehyde	KH*	3.6	6	1,4-Benzenedimethanol(86.1) <sup>d</sup>	
Acrolein	NaH*	1.2	0.3	Allyl alcohol(97)	
Methyl acrylate	NaH*	2.7	0.25	Allyl alcohol(96)	
n-Butyl acrylate	NaH*	2.7	0.25	Allyl alcohol(55.8)	
n-Butyl acrylate	NaH*	2.7	1.5	Allyl alcohol(97.7)	
Nitrobenzene	NaH <sup>b</sup>	9	50	Azoxybenzene(8)	
Nitrobenzene	NaH*	9	14	Azoxybenzene(61) aniline(17)	
1-Bromonaphthalene	NaH*	2.7	8	Naphthalene(100)	
Benzyl chloride	NaH*	4.5	4	Toluene(100)	
1,2-Dibromobenzene	NaH*	3.6	1	Bromobenzene(0) benzene(96)	
1,4-Dibromobenzene	NaH*	3.6	1	Bromobenzene(23) benzene(77)	
1,2-Dichloroethane	NaH <sup>b</sup>	2.7	9	Ethylene(7)	
1.2-Dichloroethane	NaH*	2.7	8	Ethylene(100)	

 
 Table 1. Reductions of some representative organic functional groups with various metal hydrides MH

Reaction conditions: 5 mmol substrate, refluxing in 10 mL THF, except for PhNO<sub>2</sub> at 80°C in dioxane, or for acrolein and acrylates at 20°C in dioxane. Yields were calculated by GC with internal standards, except for PhNO<sub>2</sub>, terephthalaldehyde and their products by HPLC.

a.R=MH/substrate (molar ratio), b.commercial NaH, from Germany (Serva, 2.5µm),

c. with addition of 5 mmol Ni(OAc)2, d. isolated yield.

and even in refluxing dioxane<sup>4</sup>. However, as listed in Table 1, 1-bromonaphthalene can be quantitatively reduced to naphthalene with NaH\* in refluxing THF, and even reduction of C-Cl bond to C-H bond can take place easily with 100% yield, just as benzyl chloride to toluene. 1, 2-dichloroethane gives 100% elimination product in 8h by NaH\*.

#### 2. CYCLOTRIMERIZATION:



Table 2.	Cvclo	trimeri	zation	of n	itriles	bv	Nal	Н
	- /							

Substrate	NaH*/substrate	Product (isolated yield, %)			
Benzonitrile	1:1	Triazine(34)	imidazole(27)		
<i>p</i> -Toluonitrile	2:1	Triazine(22)	imidazole(71)		
o-Toluonitrile	2:1	No reaction			

Reaction conditions: 5 mmol substrate, refluxing in 10 mL THF for 7h.

In the reaction of benzonitrile with NaH\*, only a small amount of reductive product(<3%), benzaldehyde, is formed, and unexpected cyclotrimerization of benzonitrile occurs (eq 1) with a total conversion of 98%. This result is quite similar to that of Rieke's magnesium<sup>16</sup>. In comparison, for the reaction with commercial NaH, the total conversion is only 3%. The reaction of *p*-toluonitrile shows rather high selectivity toward imidazole (see Table 2). For *o*-toluonitrile, the trimerization does not occur. A possible reason for the latter case is that the steric hindrance is too great. These results may provide a convenient way for the preparation of some 2, 4, 5-trisubstituted imidazoles.

#### 3. METALATION :

The alkali metal hydrides were used to react with an excess of dimethyl sulfoxide (DMSO) in tetrahydrofuran (THF) to measure the relative reactivities of the hydrides (eq 2). Fig.1 gives the results of metalations of DMSO at 20°C by

these highly reactive metal hydrides. The corresponding conversions of the KH\*, NaH\* and LiH\* are 100% within half a min, 86% in 10 min and 61% in 30 min, respectively. However, when the commercial alkali metal hydrides were used, KH reacted completely in 8 min at 25°C; NaH gave a conversion less than 20% even at 50°C; and LiH was inert<sup>1</sup>.

$$MH^* + CH_3 SOCH_3 \xrightarrow{THF} CH_3 SOCH_2 M^* + H_2 (eq 2)$$



Fig. 1. Conversion of reactive MH\* with excess DMSO in THF Reaction conditions: 20°C, 10 mL THF, 20 mL DMSO, 10 mmol MH.

#### **EXPERIMENTAL**

Reactions were performed in Schlenk tubes in an atmosphere of dry, oxygen free argon. Solvents were dried and distilled by the standard method. Other organic materials were purchased from commercial sources and dried with anhydrous sodium sulfate. The highly reactive alkali metal hydrides were prepared as previously described<sup>15</sup>.

Melting points were uncorrected. The reactions were monitored by GC using DEGS column (with internal standards), or HPLC on Shimadzu LC-5A liquid chromatograph using a  $C_{18}$  reversed-phase column and a UV detector (254 nm).

General procedure for the reactions with metal hydrides: To a three-necked jacketed flask (closed with a self-sealing silicon rubber septum) alternately evacuated and flushed with argon three times, the hydride (and Ni(OAc)<sub>2</sub> when needed) and 10 mL of solvent were added, then the calculated amount of organic substrate and a suitable internal standard were injected. The reaction temperature was maintained by a thermostat, and the reaction mixture was stirred magnetically. The reaction was monitored by GC or HPLC analysis of small aliquots (quenched with  $H_2O$ ) by comparison with an authentic sample.

**Reaction of terephthalaldehyde:** After the designated reaction time, the reaction mixture was quenched with  $H_2O$ , neutralized with 20%  $H_2SO_4$  and dried under reduced pressure. The solid residue was extracted repeatedly with absolute ethanol to obtain the crude product. On recrystallization from hot water 1,4-benzenedimethanol was obtained (86.1%): m.p. 114-116°C (lit.<sup>17</sup> m.p. 115-116°C).

**Reactions of nitrile compounds:** The reaction product was filtered after the reaction mixture was treated with a small amount of water, and the resulting solid (triazine) was washed with dichloromethane and then dried. The mother liquor was concentrated and the corresponding products were isolated by TLC on silica gel. The isolated products from benzonitrile were 2,4,6-triphenyl-1,3,5-triazine (34%): m.p. 232-234°C (lit.<sup>18</sup> m.p. 232°C), and 2,4,5-triphenylimidazole (27%): m.p. 274-276°C (lit.<sup>18</sup> m.p. 273°C). The products from *p*-toluonitrile were 2,4,6-tris-*p*-tolyl-1,3,5-triazine (22%): m.p. 277-279°C (lit.<sup>19</sup> m.p. 278-280°C) and 2,4,5-tris-*p*-tolylimidazole (71%): m.p. 232-233°C (lit.<sup>20</sup> m.p. 232-233°C).

Metalation of DMSO: To the similar flask alternately evacuated and flushed with argon three times, 10 mmol MH\* and 10 mL of THF were added. Then 20 mL DMSO was added dropwise. Hydrogen evolution was measured by a constant-pressure gas burette. The reaction temperature was maintained at 20°C and the reaction mixture was stirred magnetically.

Acknowledgment: We thank the National Natural Science Foundation of China and the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences for financial support.

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(Received in the USA 17 June 1997)