Tetrahedron Letters No.29, pp. 3303-3306, 1968. Pergamon Press. Printed in Great Britain.

PROPERTIES OF SODIUM-BIS-(2-METHOXYETHOXY)ALUMINIUMHYDRIDE. I. REDUCTION OF SOME ORGANIC FUNCTIONAL GROUPS

**V. Bažant, M. Čapka, M. Černý, V. Chvalovský,
K. Kochloefl, M. Kraus and J. Málek**

**Institute of Chemical Process Fundamentals, Czechoslovak
Academy of Sciences, Prague-Suchdol**

(Received in UK 8 April 1968; accepted for publication 25 April 1968)

Recently, the preparation of sodium-bis-(2-methoxyethoxy)aluminiumhydride $NaAlH_2(OCH_2CH_2OCH_3)_2$ was reported (1). This reducing reagent differs significantly from any other complex hydride by its solubility in aromatic hydrocarbons and increased stability on air; it is, therefore hoped that this new hydride may find a number of applications (2). In the present paper, we summarize the preliminary results of reduction of typical organic functional groups by sodium-bis-(2-methoxyethoxy)aluminiumhydride. Table I contains typical experimental data. The reductions were performed by the standard method common for other complex hydrides (3). The reaction mixture was then hydrolysed in the presence of an inorganic acid or base, respectivelly, according to the nature of the products. In most cases benzene was used as the solvent, bromobenzene was reduced in xylene,acyl chlorides, nitriles and N-methylsuccinimide in toluene. The yields in the reduction of aldehydes, ketones, acyl halides and alkyl and aryl halides were determined by gas chromatographic analysis of the organic layer after hydrolysis. In the case of other compounds the products were isolated by distillation or crystallisation.

The reduction of aldehydes and ketones was very rapid and almost quantitative yields were obtained. The only exception was sterically hindered 2,4,6-trimethylacetophenone which gave only 10 % yield of the corresponding alcohol, irrespectively of the conditions used. According to the arrangement of the experiment, 3-phenyl-2-propenal was reduced to 3-phenyl-2-propen-1-ol or to 3-phenylpropanol, resp. (Table I); high selectivity was observed and the obtained alcohols were free of the starting aldehyde and the latter alcohol. Weaker reducing agents, like sodiumborohydride (4) and sodiumtrimethoxyborohydride (5) gave only the unsaturated alcohol.

In the same way cinnamoylchloride and ethyl cinnamate may by reduced either partially under preservation of the carbon-carbon double bond to the unsaturated alcohol or totally to 3-phenylpropanol. Cinnamic acid gave only 3-phenylpropanol in a very low yield (5 %).

In no case was the formation of an aldehyde from an acid, ester or acyl chloride was observed even under favourable conditions (low temperature, low ratio of the hydride to the organic compounds).

The nitrile group bonded to the aromatic nucleus is easily reduced; however very unsatisfactory results were obtained with nitriles containing hydrogen atoms on the α-carbon atom, in spite of the fact that these compounds react smoothly with lithiumaluminiumhydride (6).

Sodium-bis-(2-methoxyethoxy)aluminiumhydride reduces also aliphatic and aromatic nitro compounds. In this respect it again resembles lithiumaluminiumhydride and differs from sodiumborohydride and potassiumborohydride (7). Oximes, acid anhydrides, lactones, imides and lactams gave excellent or good yields of corresponding products (see Table I). Whereas N-phenylacetamide gave N-ethylanilin in 84.5 % yield, from N-methyl-N-phenylbenzamide benzaldehyde was obtained in 66 % yield when the temperature was kept under $0^{o}C$ and the hydride added to the amide. This single example of aldehyde formation from carboxylic acid derivative may be probably due to steric hinderance.

Organohalides are reduced only by few complex hydrides; even in the case of lithiumaluminiumhydride large excess of the reagent is necessary (8). We have applied 35 % excess of sodium-bis-(2-methoxyethoxy)aluminium-

TABLE I

Experimental conditions of reduction

Compound	R [a]	Temperature, °C	Time h	Product	Yield %
Butanal	0.55	30 - 80	0.1	1-butanol	97
3-Phenyl-2-propanal	1.1	30 - 85	2	3-phenyl-1-propanol	97
3-Phenyl-2-propanal [b]	0.5	5 - 15	2.5	3-phenyl-2-propen-1-ol	94
Acetophenone	0.55	20 - 40	0.1	1-phenylethanol	95
2,4,6-Trimethylacetophenone	0.55	20 - 40	1	1-(2',4',6'-trimethylphenyl)ethanol	10
Cyclohexanoxime	4	80	1	cyclohexylamine	89
Benzoic acid	3	80	1.5	benzylalcohol	97
Nonanoylchloride	1.35	70 - 106	1	1-nonanol	82
Cinnamoylchloride	2.05	70 - 100	1	3-phenyl-1-propanol	59
Cinnamoylchloride [b]	1.05	0 - 18	1	3-phenyl-2-propen-1-ol	52
Ethyl laurate	1.2	30 - 90	0.5	1-dodekanol	98
Ethyl nicotinate	1.1	80	0.25	3-pyridylmethanol	82
Ethyl cinnamate	2.4	15 - 20	2	3-phenyl-1-propanol	44.5
Ethyl cinnamate [b]	1.1	15 - 20	0.75	3-phenyl-2-propen-1-ol	75.5
Phthalanhydride	4	80	1.5	o-phenylendimethanol	88.5
γ-Butyrolactone	1.25	80	0.3	1,4-butandiol	78.5
N-Phenylacetamide	2.25	80	2	N-ethylaniline	84.5
N-Methyl-N-phenylbenzamide	0.55	-18 - 0	1	benzaldehyde benzylalcohol	66 10.5
N-Methylsuccinimide	3	100	0.3	N-methylpyrrolidine	92
ε-Caprolactam	1.7	100	1	hexamethylenimine	81.5
Benzonitrile	2	115	4	benzylamine	81
Acetonitrile	2	115	3.5	traces of an amine	
Nitromethane	3	20 - 40	0.1	methylamine	45
Nitrobenzene	3	20 - 40	0.25	hydrazobenzene	37
1-Bromoheptane	0.68	80	1	heptane	80.5
Bromobenzene	0.68	100 - 115	1	benzene	53

[a] Molar ratio of the hydride to the organic compound. [b] Hydride added to the starting compound.

hydride with good results; this compares favourable with recomended (8) 300 % excess of lithiumaluminiumhydride. The fact that we succeeded in reducing bromobenzene in a 53 % yield also indicates high reactivity of the new hydride.

In general, the survey of reducing abilities of sodium-bis-(2-methoxyethoxy)aluminiumhydride has shown that the properties of this reagent are comparable to those of lithiumaluminiumhydride and sodiumaluminiumhydride. However, its solubility in aromatic solvents brings new possibilities. Further on, some results of the reduction of α, β-unsaturated aldehydes and acid derivatives indicate higher selectivity of $NaAlH_2(OCH_2CH_2OCH_3)_2$ in comparison with $LiAlH_4$ and $NaAlH_4$. Therefore we assume that this new hydride may find advantageous exploitation in research work as well as in the production of special organic compounds.

Detailed results of the systematic study of the new hydride will be published in the journal Collection of Czechoslovak Chemical Communications.

Acknowledgement. We wish to thank to Dr. J. Vít and his coworkers (Institute of Inorganic Syntheses, Czechoslovak Academy of Sciences, Řež near Prague) for supplying us with samples of sodium-bis-(2-methoxyethoxy)-aluminiumhydride.

References

1. J. Vít, B. Čásenský and J. Macháček, French Pat. 1 515 582.
2. V. Bažant, M. Čapka, M. Černý, V. Chvalovský, M. Kraus, J. Málek and J. Vít, Czechoslovak Pat. Appl. 667-68.
3. A. Hájos, Komplexe Hydride. Deutscher Verlag der Wissenschaften, Berlin 1966.
4. S. A. Chaikin and W. G. Brown, J. Am. Chem. Soc. **71**, 122 (1949).
5. H. C. Brown and E. J. Meal, J. Am. Chem. Soc. **75**, 6263 (1953).
6. L. H. Amudsen and L. S. Nelsom, J. Am. Chem. Soc. **73**, 242 (1951).
7. Ref. 3, p. 318.
8. J. E. Johnson, R. H. Blizzard and H. W. Carhart, J. Am. Chem. Soc. **70**, 3664 (1948).