

PROPERTIES OF SODIUM  
BIS(2-METHOXYETHOXY)ALUMINIUM HYDRIDE. XII.\*  
REDUCTION AND HYDROGENOLYSIS  
OF SODIUM AND BROMOMAGNESIUM SALTS  
OF SOME ALIPHATIC AND AROMATIC CARBOXYLIC ACIDS

M. ČERNÝ and J. MÁLEK

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

Received June 5th, 1970

The attempts to reduce the sodium salts of carboxylic acids with complex hydrides<sup>1,2</sup> have so far been unsuccessful. Only moderate yields of the corresponding alcohols were obtained in the reductions of some halomagnesium salts of aliphatic carboxylic acids with lithium aluminium hydride<sup>3</sup>.

In the present paper we wish to report the results of the investigation of the reduction of the sodium and bromomagnesium salts of aliphatic and aromatic carboxylic acids and of the reduction and hydrogenolysis of some hydroxy- and aminosubstituted aromatic carboxylic acids with sodium bis(2-methoxyethoxy)aluminium hydride. For the purpose of comparison of the reduction ability of this hydride with that of other complex hydrides, we made an attempt to reduce the sodium salts of carboxylic acids also with lithium aluminium hydride.

#### EXPERIMENTAL

##### Compounds Used

Sodium benzoate and sodium phthalate were commercial products. The sodium salts of caprylic, 10-undecenoic, stearic, and 4-aminobenzoic acids were prepared by neutralization with an alcoholic sodium hydroxide solution. After cooling, the precipitated salts were separated by filtration. The sodium salts of 4-hydroxybenzoic and 2-hydroxy-3-naphthoic acids were obtained by neutralization of the acid suspensions in water with an equivalent amount of sodium hydrogen carbonate, followed by evaporation of the filtrated solutions. The salts were dried at 110°C, pulverized and then sieved through an 0.25 mesh sieve. The sodium salt of 10-undecenoic acid was used in flaky form. The bromomagnesium salts of caproic and benzoic acids were prepared by reaction of an appropriate Grignard reagent, obtained from 1-heptyl bromide or bromobenzene in diethyl ether, with solid carbon dioxide; the suspension of the salt in diethyl ether was then directly used in the reduction. The bromomagnesium salt of benzoic acid contained 3-4% of diphenyl. The benzene solutions of sodium bis(2-methoxyethoxy)aluminium hydride (69-70%) were supplied by the Institute of Inorganic Syntheses, Czechoslovak Academy of Sciences, Prague-Řež, and were diluted with benzene or xylene, if necessary.

##### Analysis

The composition and purity of 1-octanol and benzyl alcohol isolated as the products of reduction, and of *p*-cresol, formed as the product of hydrogenolysis, were determined with the aid of authentic samples by gas-chromatographic analysis, on a Chrom I instrument equipped with

\* Part XI: This Journal 35, 3079 (1970).

a flame-ionization detector or a Pye chromatograph provided with an Argon-Pye detector. The chromatographic columns were packed with a silicone elastomer (14% on Celite). The amount of benzyl alcohol and 1-octanol freed by hydrolysis of the reaction mixture was determined with *n*-tridecane as internal standard. The other reaction products were identified and their purity checked by mixed melting points taken with authentic compounds.

#### Reduction and Hydrogenolysis

The hydride solution in benzene was added under stirring to a suspension of the sodium salt in benzene or that of the bromomagnesium salt in ether or benzene, and then the reaction mixture

TABLE I

Reduction of Sodium and Bromomagnesium Salts of Aliphatic and Aromatic Carboxylic Acids and Hydrogenolysis of Sodium Salts of Amino- or Hydroxysubstituted Aromatic Carboxylic Acids by Sodium Bis(2-methoxyethoxy)aluminium Hydride

Compound	R <sup>a</sup>	C <sup>b</sup> %	Tempe- rature °C	Time h	Product	Yield <sup>c</sup> %
Sodium benzoate	2.2	19.5	80	2	benzyl alcohol	89 <sup>d</sup>
Sodium phthalate	3	24	80	2	<i>o</i> -phenylenedimethanol <sup>e,f</sup>	37
	5	21	80	7	<i>o</i> -phenylenedimethanol <sup>e</sup>	82
	1.5	13	80	1	1-octadecanol <sup>g</sup>	96
Sodium 10-undecenoate	1.5	12	80	0.25	10-undecene-1-ol <sup>h</sup>	97.5
Sodium 4-hydroxybenzoate	4	33 <sup>i</sup>	142	8	<i>p</i> -cresol <sup>j</sup>	44
Sodium 4-aminobenzoate	5	50 <sup>i</sup>	142	3	<i>p</i> -toluidine	38 <sup>k</sup>
Sodium 2-hydroxy-3-naphthoate	3	15	80	6	3-hydroxymethyl-2-naphthol <sup>l</sup>	81
Bromomagnesium caprylate	1.8	17.5 <sup>o</sup>	35	1	1-octanol <sup>m</sup>	70 <sup>n</sup>
	1.8	16 <sup>o</sup>	80	1	1-octanol <sup>p</sup>	85 <sup>n</sup>
Bromomagnesium benzoate	1.8	20 <sup>o</sup>	80	1	benzyl alcohol	79 <sup>q</sup>

<sup>a</sup> Molar ratio of the hydride to the organic compound. <sup>b</sup> Concentration of the hydride related to the overall weight of the solvents. <sup>c</sup> Yields of the isolated products unless otherwise stated. <sup>d</sup> 99% by gas chromatographic analysis (tridecane as internal standard) of the hydrolysed reaction mixture. <sup>e</sup> B.p. 109–110°C/0.4–0.5 Torr; after crystallisation from light petroleum–benzene–ethanol m.p. 63.5–64.0°C (lit.<sup>9</sup> m.p. 64°C). <sup>f</sup> 43% of phthalic acid was isolated by acidification of the NaHCO<sub>3</sub> extract with 20% H<sub>2</sub>SO<sub>4</sub> solution. <sup>g</sup> M.p. 57.5–58.0°C (lit.<sup>10</sup> m.p. 57.85°C). <sup>h</sup> B.p. 127–8°C/11 Torr (lit.<sup>11</sup> b.p. 131–132°C/14 Torr); 0.5% of 10-undecenoic acid was isolated by the extraction of the ethereal solution with 20% KOH solution. <sup>i</sup> After partial distilling off the solvents and reaching the desired reaction temperature. <sup>j</sup> 4-Hydroxybenzoic acid (13%) was recovered. <sup>k</sup> As a hydrochloride. <sup>l</sup> Isolated by sublimation at 0.6 Torr (bath temperature 160°C); m.p. 190–191°C (lit.<sup>12</sup> m.p. 190–191°C); 12% of 2-hydroxy-3-naphthoic acid was recovered. <sup>m</sup> B.p. 85–86°C/10–11 Torr (lit.<sup>13</sup> b.p. 89.1–89.2°C/9 Torr); 13% of caprylic acid was recovered. <sup>n</sup> On the starting 1-C<sub>7</sub>H<sub>15</sub>Br. <sup>o</sup> Related to the mixture of solvents after preparation of bromomagnesium salt and addition of hydride solution. <sup>p</sup> B.p. 89–90°C/11–12 Torr. <sup>q</sup> Related to the starting C<sub>6</sub>H<sub>5</sub>Br.

was kept at chosen temperature for required time. After cooling, the reaction mixture was diluted with diethyl ether, hydrolyzed with 20% sulphuric acid, the organic layer was separated and combined with the ethereal extracts of the aqueous layer, shaken with aqueous sodium hydrogen carbonate or potassium hydroxide solutions, and then dried over anhydrous sodium sulphate. The corresponding alcohol was isolated by distillation, sublimation or crystallization. In the hydrogenolysis of the sodium salts of 4-hydroxy- and 4-aminobenzoic acids the hydride solution in benzene was added to a suspension of the salt in xylene, and the solvents were distilled off until the temperature of the reaction mixture reached 142°C. After the reaction was completed, the reaction mixture was decomposed with water; in the case of 4-hydroxybenzoic acid the diethyl ether-xylene layer was separated and the aqueous layer, after acidification with sulphuric acid, was extracted with diethyl ether. The organic layer was combined with the ethereal extracts and dried; *p*-cresol was isolated by distillation under reduced pressure; in the case of 4-aminobenzoic acid the diethyl ether-xylene layer was combined with the ethereal extracts of the aqueous layer, the mixture was shaken with 20% sulphuric acid, the acid layer was made alkaline with 50% potassium hydroxide and extracted with diethyl ether. The ethereal extracts were dried with solid potassium hydroxide and *p*-toluidine was isolated as a hydrochloride.

TABLE II

Reduction of Sodium Caprylate and Sodium Benzoate by Sodium Bis(2-methoxyethoxy)aluminium Hydride or Lithium Aluminium Hydride

Reagent	Solvent	R <sup>a</sup>	C <sup>b</sup> %	Temperature, °C	Time <sup>c</sup> min	Yield <sup>d</sup> %
Sodium caprylate						
NaAlH <sub>2</sub> (OC <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub> ) <sub>2</sub>	benzene	1	8	80	30	61
	benzene	1.2	9	80	1	70
	benzene	1.2	9	80	30	77
	benzene	1.5	11	80	1	95
	benzene	1.5	11	80	2	98
	benzene	1.5	11	80	10	99
	benzene	2	14	80	10	99
LiAlH <sub>4</sub>	tetrahydrofurane	1	2	66	5	100
Sodium benzoate						
NaAlH <sub>2</sub> (OC <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub> ) <sub>2</sub>	diethyl ether	2	18	35	60	15
	benzene	1.12	16.5	80	10	99
	benzene	1.12	16.5	80	30	100
LiAlH <sub>4</sub>	diethyl ether	1.3	2.3	35	60	76
	diethyl ether	1.3	2.3	35	240	100
	tetrahydrofurane	1.3	2.1	66	240	100

<sup>a</sup> Molar ratio of the hydride to sodium caprylate or sodium benzoate. <sup>b</sup> Concentration of the hydride related to the overall weight of the solvents. <sup>c</sup> At the boiling point of the reaction mixture.

<sup>d</sup> By gas chromatographic analysis with n-tridecane as internal standard.

## RESULTS AND DISCUSSION

The results of the reductions of the sodium and bromomagnesium salts of aliphatic and aromatic carboxylic acids as well as those of the hydrogenolysis of the sodium salts of amino- and hydroxy-substituted aromatic carboxylic acids with sodium bis(2-methoxyethoxy)aluminium hydride are summarized in Table I, along with the experimental conditions used. Except for the reduction of sodium adipate, which yielded adipic acid instead of expected 1,6-hexandiol, the obtained yields of the alcohols (80–97%) compare well with those reported for the reductions of the free acids with this reagent<sup>4,5</sup>. The successful reduction of bromomagnesium salts of the carboxylic acids obtained by the carbonation of the Grignard reagents makes it possible to prepare an alcohol containing one carbon atom more than the starting alkyl or aryl bromide without the necessity of isolating the intermediate acid. The hydrogenolysis of the salts of hydroxy- or amino-benzoic acids proceeds less readily; the yield of the corresponding cresol or toluidine is about one half of that obtained by hydrogenolysis of the free acids<sup>6,7</sup>, presumably due to an increased insolubility of the complex of these salts with the hydride.

The stoichiometry as well as optimum conditions of the reduction of carboxylic acid salts with sodium bis(2-methoxyethoxy)aluminium hydride were established with sodium caprylate and sodium benzoate (Table II). The results indicate that 1 mol of the hydride can reduce 1 mol of the carboxylic acid salt. A 12–50% excess of the hydride ensures the complete reduction at 80°C in 10–30 min reaction time. These conditions as well as stoichiometry are thus similar to those found in the reductions of the free carboxylic acids with this hydride<sup>4</sup>.

With respect to the unexpectedly smooth reduction of the carboxylic acid salts with sodium bis(2-methoxyethoxy)aluminium hydride, we repeated the reduction in two cases also with lithium aluminium hydride (Table II). In contrast to the statement<sup>8</sup> that the carboxylic acid salts cannot be reduced with this reagent, we obtained the corresponding alcohols in both cases in practically quantitative yield.

*We wish to thank Dr B. Čáseňský, Institute of Inorganic Syntheses, Czechoslovak Academy of Sciences, Prague-Řež, for supplying us with samples of sodium bis(2-methoxyethoxy)aluminium hydride.*

## REFERENCES

1. Brown H. C., Subba Rao B. S.: *J. Am. Chem. Soc.* **78**, 2582 (1956).
2. Brown H. C., Subba Rao B. S.: *J. Am. Chem. Soc.* **82**, 681 (1960).
3. Mathers A. P., Pro M. J.: *J. Am. Chem. Soc.* **76**, 1182 (1954).
4. Černý M., Málek J., Čapka M., Chvalovský V.: *This Journal* **34**, 1025 (1969).
5. Černý M., Málek J.: *This Journal* **35**, 2030 (1970).
6. Černý M., Málek J.: *Tetrahedron Letters* **1969**, 1739.
7. Černý M., Málek J.: *This Journal* **35**, 1216 (1970).
8. Hájos A.: *Komplexe Hydride*, p. 129. Deutscher Verlag der Wissenschaften, Berlin 1966.
9. Nystrom R. F., Brown W. G.: *J. Am. Chem. Soc.* **69**, 1197 (1947).
10. Meyer J. D., Reid E. E.: *J. Am. Chem. Soc.* **55**, 1577 (1933).
11. Brody F., Bogert M. T.: *J. Am. Chem. Soc.* **65**, 1077 (1943).
12. Smith W. T., Campanaro L.: *J. Am. Chem. Soc.* **74**, 1107 (1952).
13. Butler J. A. V., Ramchandani C. N., Thompson D. W.: *J. Chem. Soc.* **1935**, 282.

Translated by J. Hetflejš.