PROPERTIES OF SODIUM-BIS-(2-METHOXYETHOXY)ALUMINIUMHYDRIDE. VIII.[x]
REDUCTION AND HYDROGENOLYSIS OF SOME HYDROXY-SUBSTITUTED AROMATIC ALDEHYDES, CARBOXYLIC ACIDS, ESTERS AND CARBINOLS

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Until now, nothing has been reported about hydrogenolysis by a complex hydride in the series of hydroxy-substituted aromatic aldehydes, carboxylic acids and their esters.

In the previous papers (1,2,3,4,5) we have commented on similar reducing properties of lithiumaluminiumhydride and sodiumaluminiumhydride with sodium-bis-(2-methoxyethoxy)aluminiumhydride, nevertheless, the surprisingly high solubility of the latter in the aromatic solvents as well as its thermal stability even at temperatures as high as about 110°C led us to study in detail the behavior toward this new hydride of some compounds, whose reductions with known hydrides were so far either unsatisfactory or fully unsuccessful. In the present communication, we summarize the first results of this investigation in the series of hydroxy-substituted aromatic derivatives.

The results of reactions between sodium-bis-(2-methoxyethoxy)aluminiumhydride and the compounds mentioned above are recorded in Table I. In all cases the starting compound was added to the hydride solution in benzene, toluene or xylene and, after warming, clear solution resulted except in the case of 2-hydroxybenzyl alcohol, 2-hydroxybenzaldehyde, ethyl 4-hydroxybenzoate and 4-hydroxybenzoic acid (at 80°C). The reaction mixture was hydrolysed by ad-

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TABLE I

Experimental conditions of reduction and hydrogenolysis

Compound	R [a]	Temperature [b], °C	Time h	Product	Yield
2-Hydroxybenzoic acid [c]	5	141	7	o-cresol	88 [d]
3-Hydroxybenzoic acid [e]	4	141	2	3-hydroxybenzyl alcohol	72
4-Hydroxybenzoic acid [c]	4	106	6.5	p-cresol	85 [f]
4-Hydroxybenzoic acid [c]	5	141	2.5	p-cresol	77 [g]
Methyl 2-hydroxybenzoate	1.8	80	1	2-hydroxybenzyl alcohol	87 [h,i]
Methyl 2-hydroxybenzoate [c]	4	141	2	o-cresol	96
Ethyl 4-hydroxybenzoate [e]	2.25	80	0.25	4-hydroxybenzyl alcohol	93 [k]
Ethyl 4-hydroxybenzoate [c]	4	141	2	p-cresol	92
2-Hydroxybenzaldehyde	2	45	2	2-hydroxybenzyl alcohol	94 [l]
2-Hydroxybenzaldehyde [c]	3	141	2	o-cresol	52
4-Hydroxybenzaldehyde [c]	3	141	2	p-cresol	85
3-Methoxy-4-hydroxybenzaldehyde [c]	3	141	2	2-methoxy-p-cresol	85
2-Hydroxybenzyl alcohol [c]	3	141	7	o-cresol	85 [m]
4-Hydroxybenzyl alcohol [c]	3	141	7	p-cresol	95

[a] Molar ratio of the hydride to the organic compound. [b] All reactions performed at 80°C or at lower temperature were carried out in benzene solution and those at 141°C in solution of xylene. [c] First successful hydrogenolysis. [d] With R 3.125 and after 1 h an yield of 24% was obtained. [e] First successful reduction. [f] The reaction was carried out in toluene solution and 6% of the starting acid was recovered. With R 4 and after 7.5 h at 80°C in benzene solution, 33% of the starting acid was recovered and p-cresol was isolated in 60% yield. [g] With R 4 and after 1 h an yield of 49% was obtained and 19% of the starting material was recovered. [h] After 5 min 99% of the starting ester was reduced. [i] Ref. [6] 50% yield with $AlH_3.AlCl_3$. [k] The stated yield pertains to a crude product, m.p. 104-110°C; one recrystallisation from water gave the pure carbinol in 70% yield, m.p. 109.5-110.5°C. [l] Ref. [7] 37% yield with $NaBH_4$. [m] With R 2 and after 2 h an yield of 21% was obtained.

dition of 20% sulfuric acid, the solvent layer separated and the aqueous layer extracted with diethyl ether. The extracts and the solvent layer were combined and the products were isolated in pure form by distillation or crystallisation. Due to the instability of 4-hydroxybenzyl alcohol, the reaction mixture resulting from the reduction of ethyl 4-hydroxybenzoate at 80°C was decomposed by addition of water, treated with carbon dioxide, extracted with ether and the ether solution was worked up as above. If cresols were present in the hydrolysed reaction mixture, then the combined extracts and solvent layer were extracted with 10% potassium hydroxide and the extract was treated to obtain pure cresol in usual manner. The possible presence of neutral organic products was checked by gas chromatographic analysis of the remaining solvent layer.

The composition and purity of the products were proved by elemental analysis, gas chromatographic analysis and IR spectrographic analysis; in some cases, mixed m.p. s were taken with known substances.

Our results indicate that aromatic aldehydes, carboxylic acids, esters and carbinols, containing a hydroxy group in the ortho or para position to the carbon-oxygen grouping, undergo hydrogenolysis to ortho- or para-cresols, when they are allowed to react with sodium-bis-(2-methoxyethoxy)aluminiumhydride at temperatures about 140°C or at lower temperatures with prolonged reaction time. On the other hand, when some of these compounds as 2-hydroxybenzaldehyde or esters of 2-hydroxy- and 4-hydroxy-benzoic acid were treated for a relatively short time with the same hydride at lower temperature ($\leq$80°C), a high yield of hydroxy-substituted benzyl alcohols was obtained. In all studied cases, only pure cresol or pure carbinol resp. were isolated as single final products from the reaction mixture.

All these results support the assumption of Conover and Tarbell (8), based on successful hydrogenolysis of o- and p-amino-substituted benzenecarboxylic acids, esters and carbinols with lithiumaluminiumhydride, that hydrogenolysis requires the presence of strong electron-donating group in the ortho or para position of the benzene ring. The validity of this assumption formulated later by Gaylord (9) as vinylogy principle is further confirmed by our finding that m-hydroxybenzoic acid, treated with sodium-bis-(2-methoxyethoxy)-aluminiumhydride under hydrogenolytic conditions for the ortho and para derivatives, gave only m-hydroxybenzyl alcohol in good yield. Similar result was obtained by Conover and Tarbell (8) in reduction of m-aminobenzoic acid with large excess of lithiumaluminiumhydride. The reduction of m-hydroxybenzoic acid was performed in homogeneous solution and the incapability of the corresponding carbinol to hydrogenolyse cannot be thus explained by the insolubility of the complex formed between the hydride and the compound during the reduction. The prevailing electron-donating character of the hydroxyl group over that of the methoxyl group is well demonstrated in our case by the hydrogenolysis of 3-methoxy-4-hydroxybenzaldehyde with sodium-bis-(2-methoxyethoxy)aluminiumhydride.

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