

THE CHEMISTRY OF SODIUM ALKOXYALUMINIUM HYDRIDES. III.*
 SYNTHESIS OF SODIUM DIHYDRO-BIS(2-METHOXYETHOXY)-
 ALUMINATE FROM Na, Al, H₂ AND ALUMINIUM 2-METHOXYETHOXIDE
 OR SODIUM TETRAKIS(2-METHOXYETHOXY)ALUMINATE

B. ČÁSENSKÝ, J. MACHÁČEK and K. ABRHAM

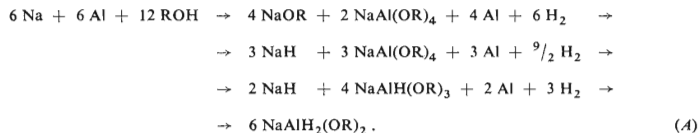
Institute of Inorganic Syntheses,

Czechoslovak Academy of Sciences, Prague-Řež

Received June 2nd, 1971

Sodium dihydro-bis(2-methoxyethoxy)aluminate (*I*) was synthesized from sodium, aluminium and either aluminium 2-methoxyethoxide (reaction (1) or sodium tetrakis(2-methoxyethoxy)aluminate (reaction (2)); the synthesis was effected in benzene under a pressure of hydrogen. In reaction (1) the primary step was the formation of aluminium and sodium tetrakis(2-methoxyethoxy)aluminate from sodium and aluminium 2-methoxyethoxide. The following steps were identical with reaction (2). Until 50% of the hydrogen had reacted there were simultaneously formed sodium hydride and sodium hydrido-tris(2-methoxyethoxy)aluminate; the succeeding reaction of these two intermediates yielded compound *I*.

The preceding paper¹ deals with the direct synthesis of sodium dihydro-bis(2-methoxyethoxy)aluminate (*I*) from sodium, aluminium and (1) aluminium 2-methoxyethoxide, (2) sodium tetrakis(2-methoxyethoxy)aluminate, or (3) 2-methoxyethanol in benzene under a pressure of hydrogen. The course of reaction (3) has been described by scheme (A):

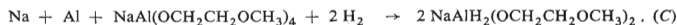
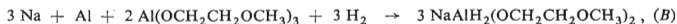


In this case only aluminium can be hydrogenated and the formation of sodium hydride was ascribed to the reactions of sodium 2-methoxyethoxide with compound *I*, sodium hydrido-tris(2-methoxyethoxy)aluminate (*II*) and aluminium hydride.

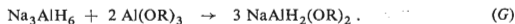
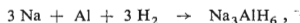
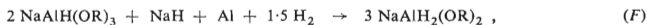
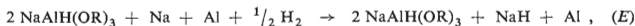
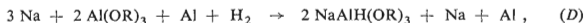
The present paper describes the syntheses of compound *I* from aluminium 2-methoxyethoxide and sodium tetrakis(2-methoxyethoxy)aluminate. We have attempted to compare these reactions with the established course of the synthesis starting from 2-methoxyethanol and to characterize their mechanisms in more detail. The

* Part II: This Journal 37, 1178 (1972).

formation of compound *I* in reactions (1) and (2) can be expressed as follows:



In either case hydrogenation of sodium and aluminium is postulated. We consider the following possible mechanisms:



According to reaction (F) hydrogenation of aluminium starts after 50% of hydrogen has reacted, whereas according to reaction (D) and (E) this hydrogenation occurs sooner; the ratio of Na to Al in the solution would equal 1 after 33% of hydrogen had reacted. With reaction (G) this ratio would equal 1 at the very end of the reaction; it has been ascertained^{2,3} that the two steps proceed very readily.

Reaction (C) implies hydrogenation of sodium and aluminium with the simultaneous formation of sodium hydride and sodium tetrahydridoaluminate. The latter reacts with sodium tetrakis(2-methoxyethoxy)aluminate and the resulting intermediate *II* is converted into compound *I*. The relation of the hydrogen consumption to time in reactions (B) and (C) is similar to that observed in the synthesis from 2-methoxyethanol; the course of the hydrogen consumption in reaction (B) is shown in Fig. 1. The lower rate of hydrogenation is due to the lower pressure of hydrogen and the smaller surface of aluminium. The individual steps of the over-all reactions were investigated by stopping them at selected stages. The synthesis proceeding according to reaction (B) was discontinued when the hydrogen consumption had reached the extent marked in Fig. 1 and the reaction mixture was analysed. The compositions of the reaction mixtures are given in Table I. The samples corresponding to low hydrogen consumptions (10.8%; 22.7%; 35.7%) contained unreacted sodium besides sodium hydride, identified by X-ray analysis. Like with reaction *A* the solid phase contained no remaining alcoholate. The ratio of sodium to aluminium was found to be 1 from the start of the hydrogenation. To account for this fact it is necessary to assume that sodium reacts with aluminium 2-methoxyethoxide, present in the reaction mixture. The assumption has been proved correct by effecting the reaction



TABLE I

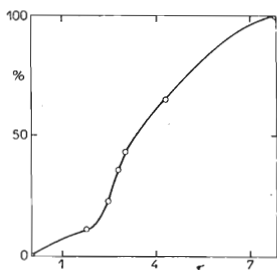
The Ratio Na : Al : H⁻ in the Synthesis of Compound *I* from Aluminium 2-Methoxyethoxide in Relation to the Reacted Hydrogen

H ₂ consumption %	Na	Al	H ⁻	H ₂ consumption %	Na	Al	H ⁻
10.8	0.991	1.000	0.240	43.3	1.031	1.000	0.867
22.7	0.991	1.000	0.517	64.9	1.012	1.000	1.337
35.7	0.984	1.000	0.768	100	0.995	1.000	1.960

FIG. 1

Hydrogen Consumption in Relation to Time (h) in the Synthesis of Sodium Dihydrido-bis(2-methoxyethoxy)aluminate from Sodium Aluminium and Aluminium 2-Methoxyethoxide

The circles designate interruption of the individual experiments.



Consequently, the behaviour of aluminium 2-methoxyethoxide towards sodium resembles that of trialkylaluminium compounds⁴. It is strange that this was not observed with aluminium ethoxide, reacting with sodium under a pressure of hydrogen with the formation of sodium hydride⁵, whose subsequent reaction on the addition of ether yields sodium hydrido-triethoxyaluminate. In the synthesis of compound *I* from aluminium 2-methoxyethoxide the mixture left from reaction *H* had, before hydrogenation, the same composition as that in the synthesis from sodium tetrakis (2-methoxyethoxy)aluminate and the rest of the reaction course was identical for syntheses 1 and 2. The data in Table II are an experimental proof of the correctness of this assumption. The summary of this process is expressed by reactions (*I*) and (*J*).

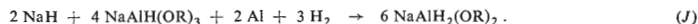
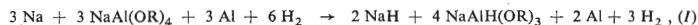
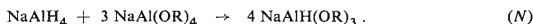
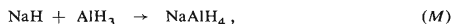
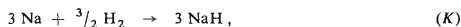


TABLE II

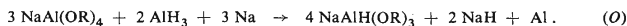
The Ratio Na : Al : H⁻ in the Synthesis of Compound I from Sodium Tetrakis(2-methoxyethoxy)aluminate in Relation to the Reacted Hydrogen

H ₂ consumption %	Na	Al	H ⁻	H ₂ consumption %	Na	Al	H ⁻
13.5	1.018	1.000	0.238	50	1.015	1.000	0.969
21	1.017	1.000	0.368	75	1.006	1.000	1.591
36	1.008	1.000	0.764	100	1.004	1.000	1.97

The two reactions differ in the hydrogenation rate only. This can be explained by the great surface of aluminium separated in the reaction of aluminium 2-methoxyethoxide with sodium. We assumed that sodium hydride and aluminium hydride were formed and reacted with the formation of sodium tetrahydroaluminate, which, in turn, reacted with sodium tetrakis(2-methoxyethoxy)aluminate, yielding compound II. Therefore, we expected that before 50% of hydrogen had reacted the following reactions would take place:



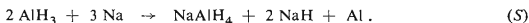
The hydrogenation rate of sodium (K) in syntheses (1) and (2) is the same as the hydrogenation rate of aluminium (L) despite the great difference in the reaction surface. This fact is best explained by the assumption that a prerequisite for the formation of sodium hydride is the formation of aluminium hydride, *i.e.* hydrogenation of aluminium:



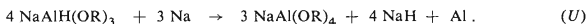
Experiment has proved the existence of this reaction, which accounts for the composition of the reaction mixture at the half consumption of hydrogen. However, reaction (O) may be the result of reactions (P) and (R):



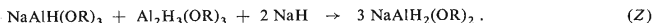
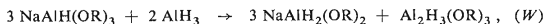
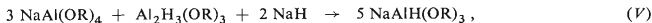
The existence of reaction (*P*) is suggested by the observation that polymeric aluminium hydride readily dissolved in a toluene solution of sodium tetrakis(2-methoxyethoxy)aluminate. The existence of reaction (*R*) has been confirmed experimentally; X-ray analysis of the solid phase demonstrated the presence of sodium hydride and aluminium. Besides reactions (*P*) and (*R*) reactions (*S*) and (*N*) also comply with the dependence of the formation of sodium hydride on the hydrogenation of aluminium:



This mechanism, however, is not so probable since a prerequisite for it is the formation of insoluble sodium tetrahydridoaluminate, entering the solution only by the succeeding reaction. Nevertheless, reaction (*S*) obviously occurs in hydrogenation of sodium and aluminium since from the start of the hydrogenation the reaction mixture contains both sodium hydride and trisodium hexahydridoaluminate⁶, whose formation we assume to be preceded by reaction (*S*). This mechanism is supported by the reaction of aluminium hydride with potassium⁷, giving rise to potassium tetrahydridoaluminate and aluminium, if we assume the simultaneous reaction of sodium tetrahydridoaluminate with sodium, yielding sodium hydride and aluminium. For the sake of completeness we have treated compounds *I* and *II* with sodium. Reactions (*T*) and (*U*), giving rise to sodium hydride and aluminium, took place.



The course of these reactions was considerably dependent on the stirring of the reaction mixture. This fact explains the presence of active hydrogen in the reaction mixture until 25% of the hydrogen had reacted. The course of the hydrogenation up to a 50% consumption of hydrogen was a series of overlapping reactions, whose result, *i.e.* compound *II* and sodium hydride, corresponds to the summary reaction (*O*). On prolonged hydrogenation of aluminium compound *II* and sodium hydride gave rise to compound *I*. The formation of the individual compounds from the intermediates can be expressed by reactions (*V*) to (*Z*).



It can be concluded that direct synthesis of sodium dihydrido-bis(2-methoxyethoxy)aluminate, under a pressure of hydrogen, from sodium, aluminium and (*I*) aluminium

2-methoxyethoxide, (2) sodium tetrakis(2-methoxyethoxy)aluminate, or (3) 2-methoxyethanol takes the same course in all cases after 50% of the hydrogen has reacted. Compound *I* is formed by reactions of sodium hydride, sodium hydrido-tris(2-methoxyethoxy)aluminate, aluminium and hydrogen; the intermediary stages are described by reactions *W* and *Z*. Up to a 50% hydrogenation the course of the synthesis is influenced by the composition of the starting mixture. The initiator of the synthesis is sodium tetrakis(2-methoxyethoxy)aluminate, whose reaction with aluminium hydride (*P*) produces the first active hydrogen, if sodium 2-methoxyethoxide is present, the soluble compounds from the insoluble sodium hydride, as the only compound containing anionic hydrogen. In the presence of sodium reactions (*R*) and (*U*) simultaneously occur. The intermediary sodium hydride is not formed by hydrogenation of sodium, but by the reaction of sodium 2-methoxyethoxide or sodium with the hydrogenation products of aluminium. Compound *II* is formed by reactions (*P*), (*R*) and (*V*). In the use of aluminium 2-methoxyethoxide the reaction of this compound with sodium yields sodium tetrakis(2-methoxyethoxy)aluminate and aluminium.

EXPERIMENTAL

Chemicals. Benzene was distilled from a solution of sodium dihydrido-bis(2-methoxyethoxy)aluminate. 2-Methoxyethanol was absolutized and distilled. The purity of sodium was 99.9%. The aluminium was in the form of a coarse powder with a surface of 0.18 m²/g. The preparation of aluminium 2-methoxyethoxide and sodium tetrakis(2-methoxyethoxy)aluminate was described previously².

Syntheses of Compound *I*; Investigation of the Reaction Course

The experiments were carried out in an agitated 200-ml pressure bottle with three steel balls at 140–150°C and a hydrogen pressure of 120–160 atm, which conditions were selected as optimum to follow the reaction course. In order to determine the amount of the reacted hydrogen two experiments were allowed to proceed until no more hydrogen reacted and the obtained sodium dihydrido-bis(2-methoxyethoxy)aluminate was analysed. The average consumption of hydrogen was taken as 100%. In the individual experiments the pressure bottle was cooled down on a selected hydrogen consumption, the pressure in the cooled bottle was read off and the reaction mixture was taken out. The solid phase was collected on a filter and washed. The filtrates were combined and analysed. With samples corresponding to low hydrogen consumptions analysis of the solid phase was made difficult by the presence of unreacted sodium, which in most cases was found on the wall of the pressure bottle. The weights of the starting chemicals were the following ones: *I*. sodium 4.6 g (0.2 mol); 98% grained aluminium, of a specific surface 0.180 m²/g, 2.75 g (0.1 mol, 50% excess); aluminium 2-methoxyethoxide 33.6 g (0.133 mol), and 50 ml of benzene 2. sodium 2.3 g (0.1 mol), 98% aluminium 4.12 g (0.15 mol, 50% excess); sodium tetrakis(2-methoxyethoxy)aluminate 35 g, (0.1 mol) and 50 ml of benzene. The working solutions of the alcoholates were prepared from stock solutions in benzene.

Reaction of Aluminium 2-Methoxyethoxide with Sodium

The pressure bottle was charged with aluminium 2-methoxyethoxide (32.8 g, 130 mmol) in 38 ml of benzene and metallic sodium (1.5 g, 65 mmol). The pressure in the bottle was brought to 8 atm with nitrogen. In the course of 25 min the temperature of the reaction mixture was elevated to 140–150°C, at which value it was maintained for another 25 min. The bottle was then cooled down under agitation and deaerated, the black suspension was poured out and allowed to sediment. The presence of aluminium in the suspension was detected by X-ray analysis. The calculated content of sodium in the solution was 2.25%, the determined value was 2.17%.

Reaction of Sodium Tetrakis(2-methoxyethoxy)aluminate and Aluminium Hydride with Sodium

To a solution obtained by mixing sodium tetrakis(2-methoxy-ethoxy)aluminate (56.96 g, 0.16 mol) in toluene (100 ml) with aluminium hydride (1.41 g, 0.47 mol) in diethyl ether (45 ml) was added metallic sodium (1.62 g, 0.07 mol). The boiling reaction mixture was stirred with a spiral while diethyl ether was distilled off. (Immediately on raising the temperature, even before sodium was mixed up, the reaction mixture turned black with the separated aluminium.) When the boiling temperature rose to 108°C the Liebig condenser was replaced with a reflux condenser. The total reaction time was 4.5 h. The solid matter (12.1 g) was then collected on a filter and the clear filtrate (128 g) was analysed. Calculated: 3.92% Al, 3.34% Na, 0.073% H⁻; found: 3.92% Al, 3.46% Na, 0.063% H⁻. The solid phase contained aluminium and sodium hydride (X-ray analysis).

REFERENCES

1. Čásenský B., Macháček J., Abrham K.: This Journal, in press.
2. Čásenský B., Macháček J., Abrham K.: This Journal, in press.
3. Hanzlík T., Mamula M.: Czechoslov. Pat. N. 117 768.
4. Zakharkin L. J., Gavrilenko V. V.: Ž. Obšč. Chim. 32, 689 (1962).
5. Smitz - Du Mont O., Nabernickel V.: Chem. Ber. 90, 1054 (1957).
6. Hanzlík T.: Unpublished results.
7. Zakharkin L. J., Gavrilenko V. V.: Ž. Neorgan. Chim. 11 (5), 977 (1966).

Translated by J. Salák.