Journal of Organometallic Chemistry, 224 (1982) 13—20
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CALCIUM ALKOXYALANATES

II *. ADVANCES IN THE SYNTHESIS

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(Received July 31st, 1981)

Summary

Simple syntheses of calcium alkoxyalanates starting from $NaAlH_4$, $CaCl_2$ and alcohols involving evolution of hydrogen and separation of sodium chloride are reported. More complex methods, which allow the preparation of calcium alkoxylalanates without loss of hydride hydrogen from $NaAlH_4$, $CaCl_2$, NaOR and AlX_3 (X = OR, Cl) have also been developed.

Introduction

In the preceding paper [1] we reported the synthesis of calcium alkoxyalanates by alcoholysis of calcium alanate tetrahydrofuran with various branched aliphatic alcohols (eq. 1), as well as some of their physicochemical properties.

$$Ca(AlH_4)_2 + 2\,n ROH \rightarrow Ca[AlH_{4-n}(OR)_n]_2 + 2\,n H_2 \qquad (1)$$

With a few exceptions these compounds are individual molecular species, and some of them have been found to be good multipurpose reducing agents for organic chemistry [2]. However, reaction 1 is not a wholly satisfactory method of synthesis because:

(i) Preparation and purification of the starting calcium alanate, which is not available commercially, are difficult.

(ii) Hydride hydrogen is partly lost as molecular hydrogen.

This prompted us to look for improved routes, with emphasis on the preparation of calcium tetrakis(alkoxy)alanates, which represent a satisfactory balance between high hydride hydrogen content, good stability, and solubility in various organic solvents. These improvements are the subject of this paper.

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Results and discussion

1. Synthesis of calcium alkoxyalanates from $NaAlH_4$, $CaCl_2$ and alcohols

Reaction 2 provides an alternative route for synthesizing calcium alkoxyalanate starting from available materials. Sodium alanate is produced as an intermediate in the industrial synthesis of poly(*N*-isopropyliminoalane), a cocatalyst for the isoprene polymerization process [3]. It can be used for reaction 2 without separation from the NaCl which is formed as by-product, according to reaction 3.

$$2\ NaAlH_4 + CaCl_2 + 2\ n\text{ROH} \rightarrow \underset{\text{(I)}}{Ca[AlH_{4-n}(OR)_n]_2} + 2\ NaCl + 2\ nH_2 \qquad (2)$$

$$4\ NaH + AlCl_3 \rightarrow NaAlH_4 + 3\ NaCl \qquad (3)$$

Unseparated sodium chloride lowers the reaction rate, but does not affect the nature of the calcium alkoxyalanates obtained.

As shown in Table 1, most of our attention was devoted to the application of reaction 2 to the synthesis of calcium tetrakis(alkoxy)alanates. However, the method is also suitable for the preparation of calcium alkoxyalanates corresponding to various degrees of alcoholysis (see run 4).

The reaction generally takes place readily in toluene or ethereal solvents in the presence of THF. A quantity of THF close to that required for the formation of molecular complexes with I is sufficient. As in reaction 1, THF complexes are preferentially formed. Reaction 2 is accelerated by the presence of an excess of $CaCl_2$. It can be monitored by observing the gradual rise in the calcium/aluminum ratio in the reaction solution; care must be taken that this ratio does not exceed the theoretical 0.5, otherwise the excess $CaCl_2$ slowly complexes with the product calcium alkoxyalanates.

2. Synthesis of calcium alkoxyalanates from $Ca(AlH_4)_2$, $CaCl_2$, aluminum alcoholates and sodium alcoholates

Further efforts were directed towards reactions which avoid the less of the hydride hydrogen of the starting alanates. The reaction, 4, between calcium alanate, calcium chloride, aluminum alcoholates and sodium alcoholates leads to calcium alkoxyalanates.

$$x\text{Ca}(AlH_4)_2 + y\text{CaCl}_2 + 2y\text{NaOR} + 2y\text{Al(OR)}_3 \rightarrow z\text{Ca}[AlH_{4-n}(OR)_n]_2 + 2y\text{NaCl} \qquad (4)$$

$$z = x + y; \qquad n = \frac{4y}{z}$$

The simpler exchange reaction using aluminum alcoholates and calcium alcoholates was not studied, because preparations of calcium alcoholates other than those from methanol and ethanol have been little studied [4], and these latter alcoholates can be expected [1] to yield calcium alkoxyalanates with a tendency to disproportionation.

Table 2 lists the results for the preparation of calcium tetrakis(alkoxy)alanates ($x = 1$; $y = 1$; $n = 2$) and pentakis(alkoxy)alanate ($x = 3$; $y = 5$; $n = 2.5$) in high yields. Some excess $CaCl_2$ was used, and product formation was monitored by observing the calcium/aluminum ratio in the reaction solution.

3. Synthesis of calcium alkoxyalanates from $NaAlH_4$, $CaCl_2$, AlX_3 ($X = OR$, Cl) and sodium alcoholates

Despite the advantage of avoiding the loss of hydride hydrogen of the starting alanate, the use of calcium alanate limits the application of reaction 4 on a large scale. This limitation is avoided by reaction 5, which yields calcium alkoxyalanates without loss of hydride hydrogens and uses commercially or industrially available materials in addition to sodium and aluminum alcoholates.

$$2x\mathrm{NaAlH_4} + z\mathrm{CaCl_2} + 2y\mathrm{NaOR} + 2y\mathrm{Al(OR)_3} \rightarrow z\mathrm{Ca[AlH_{4-n}(OR)_n]_2} + 2z\mathrm{NaCl}$$

$$z = x + y; \qquad n = \frac{4y}{z} \tag{5}$$

Table 3 shows the conditions and the results for the preparation of calcium tris(t-butoxy)alanates ($x = 5$; $y = 3$; $n = 1.5$), calcium tetrakis(alkoxy)alanates ($x = 1$; $y = 1$; $n = 2$). Calcium pentakis(methoxyethoxy)alanate ($x = 3$; $y = 5$; $n = 2.5$) was also prepared by this method.

Reaction 5 occurs in various solvents in the presence of a minimum amount of THF close to that required for the formation of complexes with calcium alkoxyalanates.

Reaction 6 offers an alternative to reaction 5; in this reaction aluminium alcoholates are replaced by stoichiometric amounts of aluminum chloride and sodium alcholates in tetrahydrofuran.

$$2x\mathrm{NaAlH_4} + z\mathrm{CaCl_2} + 8y\mathrm{NaOR} + 2y\mathrm{AlCl_3} \rightarrow z\mathrm{Ca[AlH_{4-n}(OR)_n]_2} + (2x + 8y)\mathrm{NaCl}$$

$$z = x + y; \qquad n = \frac{4y}{z} \tag{6}$$

Examples of the preparation of calcium tris- and tetrakis(alkoxy)alanates by this reaction ($x = 5$; $y = 3$; $n = 1.5$ and $x = 1$; $y = 1$; $n = 2$, respectively) are shown in Table 3 (runs 7 and 8).

Excess $CaCl_2$ was also used in reactions 5 and 6 to enhance the reaction rate. The product formation was monitored by noting the increase in the Ca/Al ratio in the reaction solution.

Experimental

Reagents and solvents

$Ca(AlH_4)_2$ was prepared as previously reported [5] by published methods [6]. $NaAlH_4$, 90% purum was the Fluka product. Otherwise $NaAlH_4/NaCl$ (molar ratio ca. 1/3) produced industrially [3] by ANIC was used. The $CaCl_2$ powder used was the C. Erba 92% commercial product, and the $AlCl_3$ was the purist grade supplied by Fluka. Sodium and aluminum alcoholates were prepared from metals and alcohols. Commerically supplied pure alcohols were dried over molecular sieves and/or CaH_2 and distilled. All solvents were purified and dried by standard methods. All the syntheses were carried out under nitrogen.

(continued on p. 18)

TABLE 1

RESULTS OBTAINED IN THE SYNTHESIS OF CALCIUM ALKOXYALANATES BY REACTION OF $NaAlH_4$, $CaCl_2$ AND ROH [a]

Run	Reagents			Reaction conditions					Reaction product								
	$NaAlH_4$ (mmol)	$CaCl_2$ (mmol)	Alcohol (mmol)	Solvent		T (°C)	Time (h)	Yield (%)	Chemical Composition, Found (Calcd.)								
				Nature	(ml)				Al (%)	Ca (%)	Cl (%)	Na (%)	$H_{act.}$ [b]	Ca/Al	Cl/Al	Na/Al	$H_{act.}$/Al
1	65.5	60	i-C_3H_7OH (131)	THF	70	50	4	85	11.9 (11.3)	8.4 (8.4)	traces —	traces —	9.2 (8.4)	0.48 (0.50) [c]	— —	— —	2.08 (2.00)
2	69.0	69	i-C_3H_7OH (132)	Toluene THF	100 30	85	1	84	13.6 (13.3)	10.3 (9.9)	traces —	traces —	10.2 (9.9)	0.51 (0.50) [d]	— —	— —	2.02 (2.00)
3	80.0	70	i-C_3H_7OH (158)	Toluene THF	110 25	25	2	84	13.7 (13.3)	10.1 (9.9)	0.6 —	n.d. —	9.9 (9.9)	0.50 (0.50) [d]	0.03 —	— —	1.95 (2.00)
4	45.5	54	i-C_4H_9OH (68)	Toluene THF	40 40	60	6	87	14.7 (13.8)	11.0 (10.3)	n.d —	0.03 —	13.5 (12.9)	0.50 (0.50) [e]	— —	0.002 —	2.48 (2.50)
5	66.0	65	i-C_4H_9OH (130)	THF	80	50	3	95	12.0 (11.7)	9.0 (8.7)	1.1 —	0.06 —	9.1 (8.7)	0.50 (0.50) [d]	0.07 —	0.006 —	2.05 (2.00)
6	72.0	145	i-C_4H_9OH (140)	Et_2O THF	120 10	35	5	94	13.4 (13.8)	9.9 (10.3)	traces —	traces —	9.5 (10.3)	0.50 (0.50) [f]	— —	— —	1.91 (2.00)
7	66.0	75	i-C_4H_9OH (130)	Toluene THF	120 25	70	10	86	12.5 (11.7)	9.2 (8.7)	0.3 —	0.06 —	9.1 (8.7)	0.49 (0.50) [d]	0.02 —	0.006 —	1.96 (2.00)
8	78.0	75	i-$C_5H_{11}OH$ (156)	THF	80	50	3	90	11.2 (12.1)	8.1 (9.0)	traces —	0.05 —	8.1 (9.0)	0.49 (0.50) [f]	— —	0.005 —	1.95 (2.00)

[a] Except run 1, a mixture of $NaAlH_4$ and NaCl (molar ratio 1 : 3) was used. The reaction started by a slow dropping (ca. 30 minutes) of toluene (runs 2, 3, 4, 7), ether (6) or THF solution of alcohol in the stirred suspension of other starting materials. [b] H_{act} indicates hydride hydrogen content as meq/g. [c] Calcd. for $Ca[AlH_2(OR)_2]_2 \cdot 2\,THF$. [d] Calcd. for $Ca[AlH_2(OR)_2]_2 \cdot THF$. [e] Calcd. for $CaAl_2H_5(OR)_3$. [f] Calcd. for $Ca[AlH_2(OR)_2]_2$.

TABLE 2

RESULTS OBTAINED IN THE SYNTHESIS OF CALCIUM ALKOXYALANATES BY REACTION OF $Ca(AlH_4)_2$, $CaCl_2$, $Al(OR)_3$ AND NaOR

Run	Reagents				Reaction conditions				Reaction product					
	$Ca(AlH_4)_2$[a] (mmol)	$CaCl_2$ (mmol)	NaOR (mmol)	$Al(OR)_3$ (mmol)	Solvent		T(°C)	Time (h)	Yield (%)	Chemical Composition. Found (Calcd.)				
					Nature	(ml)				Al (%)	Ca (%)	$H_{act.}$[b]	Ca/Al	$H_{act.}$/Al
1	36.3	47	$NaO\text{-}i\text{-}C_3H_7$ (72.6)	$Al(O\text{-}i\text{-}C_3H_7)_3$ (72.6)	THF	200	reflux	18	95	11.5 (11.3)	8.1 (8.4)	8.1 (8.4)[c]	0.47 (0.50)	1.90 (2.00)
2	20.8	29	$NaOC_6H_{11}$ (41.6)	$Al(OC_6H_{11})_3$ (41.6)	THF	165	reflux	12	95	8.6 (8.4)	5.9 (6.3)	6.1 (6.3)[c]	0.46 (0.50)	1.91 (2.00)
3	10.0	25	$NaOC_6H_{11}$ (33.3)	$Al(OC_6H_{11})_3$ (33.3)	THF	170	reflux	1.5	93	6.7 (6.7)	5.0 (4.9)	3.7 (3.7)[d]	0.50 (0.50)	1.49 (1.50)

[a] $Ca(AlH_4)_2 \cdot 4$ THF was used as starting material. [b] $H_{act.}$ indicates hydride hydrogen content as meq./g. [c] Calcd. for $Ca[AlH_2(OR)_2]_2 \cdot 2$ THF. [d] Calcd. for $CaAl_2H_3(OR)_5 \cdot 3$ THF.

TABLE 3

RESULTS OBTAINED IN THE SYNTHESIS OF CALCIUM ALKOXYALANATES FROM NaAlH4, $CaCl_2$, NaOR AND AlX_3 (X = OR, Cl)

Run	Reagents [a]				Reaction conditions	
	$NaAlH_4$ [b] (mmol)	$CaCl_2$ (mmol)	NaOR (mmol)	AlX_3 (mmol)	Solvent	
					Nature	(ml)
1	36.0	50	$NaO\text{-}i\text{-}C_3H_7$ (35)	$Al(O\text{-}i\text{-}C_3H_7)_3$ (35)	THF	160
2	41.0	60	$NaO\text{-}i\text{-}C_3H_7$ (40)	$Al(O\text{-}i\text{-}C_3H_7)_3$ (40)	MTB [e] THF	120 20
3	52.0	70	$NaO\text{-}i\text{-}C_3H_7$ (50)	$Al(O\text{-}i\text{-}C_3H_7)_3$ (50)	Toluene THF	130 20
4	25.0	40	$NaO\text{-}t\text{-}C_4H_9$ (15)	$Al(O\text{-}t\text{-}C_4H_9)_3$ (15)	THF	130
5	20.0	20	$NaO\text{-}t\text{-}C_4H_9$ (20)	$Al(O\text{-}t\text{-}C_4H_9)_3$ (20)	Toluene THF	120 10
6	21.0	52	$NaOCH_2CH_2OCH_3$ (35)	$Al(OCH_2CH_2OCH_3)_3$ (35)	THF	140
7	11.9	17.8	$NaO\text{-}i\text{-}C_3H_7$ (47.5)	$AlCl_3$ (11.9)	THF	95
8	26.0	36	$NaO\text{-}t\text{-}C_4H_9$ (60)	$AlCl_3$ (15)	THF	145

[a] Generally, AlX_3 solution was slowly added to a stirred suspension of other reagents and the mixture was stirred until reaction was completed (further details are given in the Experimental). [b] Except for run 1, a mixture of $NaAlH_4 \cdot NaCl$ (molar ratio ca. 1 : 3) was used. [c] H_{act} indicates hydride hydrogen content as meq/g. [d] Calcd. for $Ca[AlH_2(OR)_2]_2 \cdot 2$ THF. [e] MTB is methyl t-butyl ether. [f] Calcd. for $Ca[AlH_2(OR)_2]_2 \cdot$ THF. [g] Calcd. for $CaAl_2H_5(OR)_3 \cdot 2$ THF. [h] Calcd. for $CaAl_2H_3(OR)_5$.

Chemical analyses

The chemical analyses for aluminum and calcium were performed on solutions obtained by decomposition of weighed samples with diluted aqueous acid solutions. The aluminum content was determined by the EDTA/$ZnSO_4$ method. After complexation with triethanolamine, direct titration by EDTA at pH > 12 gave the calcium content. The hydride hydrogen content was determined by the measurement of hydrogen liberated upon decomposition of a weighed sample with small amounts of n-octyl alcohol and then with aqueous 50% H_2SO_4 in a flask directly connected to the gas volumetric apparatus.

Synthesis of calcium alkoxyalanates

Typical preparations are reported for each methods

(a) Synthesis of $Ca[AlH_2(OCH(CH_3)_2)_2]_2 \cdot$ THF from $NaAlH_4$ $CaCl_2$ and $i\text{-}C_3H_7OH$. $CaCl_2$ (60 mmol) was added to a suspension (70 ml) of $NaAlH_4$ (65.5 mmol mixed to 205 mmol of NaCl) in tetrahydrofuran. A solution of i-propanol (131 mmol) in tetrahydrofuran (30 ml) was then added dropwise to the stirred refluxing mixture. Hydrogen evolution took place immediately, and was controlled by the rate of addition of the alcohol. The mixture was stirred and refluxed until the Ca/Al ratio in the solution was ca. 0.5, and was

		Reaction product							
T(°C)	Time (h)	Yield (%)	Chemical Composition, Found (Calcd.)						
			Al (%)	Ca (%)	Cl (%)	$H_{act.}$ [c]	Ca/Al	Cl/Al	$H_{act.}$/Al
reflux	8.5	88	11.6 (11.3)	8.7 (8.4)	0.8 —	9.0 (8.4) [d]	0.50 (0.50)	0.05 —	2.09 (2.00)
reflux	4.5	92	12.1 (13.3)	9.0 (9.9)	traces —	8.9 (9.9) [f]	0.50 (0.50)	— —	1.98 (2.00)
60	5.5	94	13.6 (13.3)	9.9 (9.9)	traces —	10.3 (9.9) [f]	0.49 (0.50)	— —	2.04 (2.00)
25	6	82	11.7 (11.7)	8.5 (8.7)	0.9 —	11.1 (10.9) [g]	0.49 (0.50)	0.06 —	2.56 (2.50)
80	7	40	10.4 (10.1)	7.3 (7.5)	traces —	7.5 (7.5) [d]	0.47 (0.50)	— —	1.95 (2.00)
reflux	7	80	12.0 (11.4)	8.9 (8.5)	traces —	6.7 (6.4) [h]	0.50 (0.50)	— —	1.51 (1.50)
25 reflux	1 0.5	85	12.4 (11.3)	8.8 (8.4)	traces —	8.4 (8.4) [d]	0.48 (0.50)	— —	1.83 (2.00)
reflux	18	87	10.8 (11.7)	8.3 (8.7)	traces —	10.1 (10.9) [g]	0.52 (0.50)	— —	2.52 (2.50)

then filtered. The solution was evaporated in vacuo, and the white solid residue was dried (2 h, room temperature, 1 × 10^{-2} Torr) and analyzed.

Found: Al, 11.9; Ca, 8.4%; H_{active}/Al, 2.08. $C_{20}H_{48}Al_2CaO_6$ calcd.: Al, 11.3; Ca, 8.4%; H_{active}/Al, 2.00. The yield was 85%.

(b) Synthesis of $Ca[AlH_{1.5}(OC_6H_{11})_{2.5}]_2 \cdot 3$ *THF from* $Ca(AlH_4)_2$, $CaCl_2$, $NaOC_6H_{11}$ *and* $Al(OC_6H_{11})_3$. A solution of $Ca(AlH_4)_2$ (10 mmol) in tetrahydrofuran (70 ml) was added slowly to a stirred suspension of $CaCl_2$ (25 mmol), $NaOC_6H_{11}$ (33.3 mmol) and $Al(OC_6H_{11})_3$ (33.3 mmol) in THF (100 ml). The mixture was stirred and refluxed until the Ca/Al ratio in the solution was ca. 0.50 (1.5 h). The mixture was then filtered, and the filtrate was evaporated in vacuo to give a white solid residue, which was dried (2 h, room temperature, 1 × 10^{-2} Torr) and analyzed.

Found: Al, 6.7; Ca, 5.0%; H_{active}/Al, 1.49. $C_{42}H_{82}Al_2CaO_8$ calcd.: Al, 6.7; Ca, 4.9%; H_{active}/Al, 1.50. The yield was 93%.

(c) Synthesis of $Ca[AlH_2(OC(CH_3)_3)_2] \cdot 2$ *THF from* $NaAlH_4$, $CaCl_2$, *NaO-t-*C_4H_9 *and Al(O-t-*$C_4H_9)_3$. A solution of $Al[OC(CH_3)_3]_3$ (20 mmol) in toluene (50 ml) was added slowly to a stirred suspension of $NaAlH_4$ (20 mmol mixed with ca. 60 mmol of NaCl), $CaCl_2$ (20 mmol) and $NaOC(CH_3)_3$ (20 mmol) in toluene (70 ml) and THF (10 ml). The mixture was heated at 80°C and stirred

until the Ca/Al ratio in the solution was 0.47. The mixture was then filtered and the filtrate was evaporated in vacuo to give a white solid, residue which was dried (2 h, room temperature, 1 X 10^{-2} Torr) and analyzed.

Found: Al, 10.4; Ca, 7.3%; H_{active}/Al, 1.95. $C_{24}H_{56}Al_2CaO_6$ calcd.: Al, 10.1; Ca, 7.5%; H_{active}/Al, 2.00. The yield was 40%.

(d) Synthesis of $Ca[AlH_2(OCH(CH_3)_2]_2 \cdot THF$ *from* $NaAlH_4$, $CaCl_2$, $AlCl_3$ *and* $NaO\text{-}i\text{-}C_3H_7$. A solution of $AlCl_3$ (11.9 mmol) in tetrahydrofuran (30 ml) was added slowly to a stirred suspension of $NaAlH_4$ (11.9 mmol mixed to ca. 36 mmol of NaCl), $CaCl_2$ (17.8 mmol) and $NaOCH(CH_3)_2$ (47.5 mmol) in tetrahydrofuran (65 ml). The mixture was stirred at room temperature (1 h) under reflux (0.5 h) until the Ca/Al ratio in the solution was 0.48. The mixture was then filtered, and the filtrate was evaporated in vacuo to give a white solid residue, which was dried (2 h, room temperature 1 X 10^{-2} Torr) and analyzed.

Found: Al, 12.4; Ca, 8.8%; H_{active}/Al, 1.83. $C_{20}H_{48}Al_2CaO_5$ calcd.: Al, 11.3; Ca, 8.4%; H_{active}/Al, 2.00. The yield was 85%.

Acknowledgements

The authors are grateful to ANIC for financial support and to the ASSORENI management for allowing publication.

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