

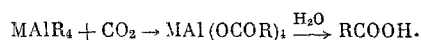
STUDY OF THE CARBOXYLATION OF TETRAALKYL COMPLEXES OF ALUMINUM MAIR₄

L. I. Zakharkin, V. V. Gavrilenko,
and V. K. Golubev

UDC 542.91:541.49

In studies on the carboxylation of aluminum trialkyls it was shown that the carboxylation of aluminum alkyls proceeds stepwise, with the formation of alkylaluminum mono- and dicarboxylates [1-4]. The third Al-C bond does not react even under drastic conditions. The LiAl(C₂H₅)₄ complex when treated with CO₂ is converted to propionic acid and diethyl ketone [5]. In contrast to these data, the reaction of CO₂ with the tetraacetylide complexes of aluminum of type MAI(C≡CR)₄ proceeds under comparatively mild conditions, with yields as high as 90% of the corresponding acids [6]. In view of this, it seemed interesting to us to make a more detailed study of this reaction on the example of the tetraalkyl compounds of aluminum of type MAIR₄ (M = Li, Na; R = C₂H₅, n-C₆H₁₃, n-C₇H₁₅, n-C₈H₁₇, n-C₁₀H₂₁).

The reaction was studied in a wide range of pressures (from normal to 230 atm) and temperatures (from 25 to 220°), using ether, aliphatic, aromatic and mixed solvents. The obtained experimental data are given in Table 1. From these data it follows that the main product from the reaction of CO₂ and MAIR₄ are carboxylic acids, the yield of which under the optimum conditions reaches 87%, i.e., the fourth Al-C bond is also partially involved in the reaction



The degree of conversion of the Al-C bonds of the tetraalkyl complex depends primarily on the reaction temperature. Thus, two Al-C bonds react at 25-135°. In the case of NaAlR₄ an increase in the temperature up to 180-220° enables achieving conversion of the third bond and, partially, of the fourth Al-C bond. In this connection the conversion (reaction of Al-C bonds) of the tetraalkyl complex reaches 87-95%. The lithium derivatives LiAlR₄ react more slowly with CO₂; at 200° not more than 70% of the Al-C bonds of the complex react in 17 h.

The high yield of carboxylic acids (82-91% when based on reacted MAIR₄) testifies to the high selectivity of the carboxylation reaction. Besides the carboxylic acids, we detected the corresponding dialkyl ketones (5-8%) and paraffins (6% and more) in the reaction products after hydrolysis. The yield of carboxylic acids and the degree of conversion of the tetraalkyl complexes are but slightly dependent on the nature of the employed solvent. On the basis of the previously published communications [1-6] and the data of the present study it must be assumed that the reactivity of organoaluminum compounds when reacted with CO₂ increases with increase in the polarity of the Al-C bonds in the series: AlR₃ < LiAlR₄ < NaAlR₄ < MAI(C≡CR)₄.

EXPERIMENTAL

The reaction of the tetraalkyl complexes MAIR₄ with CO₂ was run at atmospheric pressure in a glass reactor equipped with a stirrer, while at elevated pressure it was run in a rotated autoclave. In all of the experiments a 4-6-fold amount of CO₂ was added to the reaction directly from a cylinder. The degree of conversion of the higher tetraalkyl complexes was determined from the decrease in the concentration of the corresponding paraffin in the hydrolysis products of the reaction mixture when compared with the original concentration. The amount of paraffin in the hydrolysis product, corresponding to the unreacted MAIR₄, was determined by GLC. The analysis was run on a "Tswett-2" chromatograph at 80-100°, using a column with a diameter of 1.2 mm and a length of 3 m, and 20% PEG-20,000 deposited on Celite 545.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 7, pp. 1564-1565, July, 1971. Original article submitted July 17, 1970.

© 1972 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.

TABLE 1

| MAIR ₄ | Reaction conditions | | | | Degree of MAIR ₄ conversion, % | Yield of acid RCOOH, in % to MAIR ₄ |
|---|---------------------|--------|---------|----------------|---|--|
| | T, °C | p, atm | time, h | solvent | | |
| NaAl(C ₂ H ₅) ₄ | 50 | 1 | 4 | Toluene | 57,5 | 47 |
| NaAl(C ₈ H ₁₇) ₄ | 135 | 1 | 3 | Decane | 47,5 | 41 |
| NaAl(C ₂ H ₅) ₄ | 25 | 70 | 2 | Toluene | 48,0 | 42 |
| NaAl(C ₂ H ₅) ₄ | 150 | 100 | 3 | The same | 95 | 87 |
| NaAl(C ₂ H ₅) ₄ | 100 | 70 | 4,0 | Ether | 54 | 49 |
| NaAl(C ₆ H ₁₃) ₄ | 165 | 200 | 5 | Octane - ether | 67 | 56 |
| NaAl(C ₇ H ₁₅) ₄ | 160 | 210 | 18 | The same | 70 | 57 |
| NaAl(C ₈ H ₁₇) ₄ | 180 | 130 | 10 | Decane | 89,5 | 79,0 |
| NaAl(C ₆ H ₁₃) ₄ | 180-190 | 230 | 10 | Octane - ether | 91,6 | 78,5 |
| NaAl(C ₆ H ₁₃) ₄ | 210-220 | 160 | 16 | The same | — | 70 |
| NaAl(C ₂ H ₅) ₄ | 200 | 220 | 12 | Ether | 94,4 | 84 |
| LiAl(C ₁₀ H ₂₁) ₄ | 200 | 220 | 4 | Octane - ether | 62 | 56 |
| LiAl(C ₁₀ H ₂₁) ₄ | 200 | 230 | 17 | The same | 70 | 52 |
| LiAl(C ₇ H ₁₅) ₄ | 195 | 210 | 10 | " " | 82 | 76 |

* Octane - ether ratio, 1:4.

Reaction of NaAl(C₂H₅)₄ with CO₂. A solution of 0.131 mole of NaAl(C₂H₅)₄ in 50 ml of anhydrous ether was loaded into a rotated 0.5 liter autoclave and saturated with CO₂ up to 50-60 atm. Here the reaction mixture warmed up to 40-45°. The autoclave was heated at 200° for 12 h. The maximum pressure was 230 atm. After cooling, the reaction mass was dumped and the ether was distilled off. The residue was treated with 10% HCl solution. Here 0.66 liter (5.6%) of C₂H₆ was evolved. The propionic acid was isolated from the hydrolysis product by repeated extraction with ether. The ether layer was dried over Na₂SO₄ and fractionally distilled. We obtained 32.5 g of propionic acid with bp 140-140.8°; n_D²⁴ 1.3868; the yield of the acid was 84% when based on the starting tetraalkyl complex. We also obtained 1.8 g of diethyl ketone with bp 101-103° (760 mm); n_D²⁰ 1.3918.

Reaction of NaAl(C₆H₁₃)₄ with CO₂. A solution of 0.066 mole of NaAl(C₆H₁₃)₄ in 50 ml of octane and 50 ml of ether was treated with CO₂ in the same manner as in the preceding experiment, at 180-190° and a pressure of 230 atm for 10 h. The reaction product was hydrolyzed with 10% HCl solution. The conversion of the tetraalkyl complex was 91.6%. After separating the aqueous layer, the ether-hydrocarbon layer was treated with 8-10% alkali solution. The alkaline extracts were acidified, and the enanthic acid was extracted with ether. We isolated 26.8 g of enanthic acid (bp 104-106° (6 mm); n_D²⁰ 1.4222) in 78.5% yield (when based on the starting tetraalkyl complex). From the ether-hydrocarbon layer was isolated 2.1 g of a high-boiling product (bp 114-118° (6 mm); n_D²⁰ 1.4280).

Using the described method, pelargonic acid and undecanoic acids were synthesized from sodium tetraoctylaluminate and lithium tetradecylaluminate.

CONCLUSIONS

The reaction of the tetraalkyl complexes of aluminum (MAIR₄) with carbon dioxide was studied. In this reaction more than 3 Al-C bonds react with the formation of carboxylic acids.

LITERATURE CITED

1. L. I. Zakharkin and V. V. Gavrilenko, USSR Patent No. 112349 (February 1, 1957).
2. L. I. Zakharkin and V. V. Gavrilenko, Dokl. Akad. Nauk SSSR, **118**, 713 (1958).
3. K. Ziegler, Angew. Chem., **68**, 721 (1956).
4. K. Ziegler, F. Krupp, K. Weyer, and W. Larbig, Ann. Chem., **629**, 251 (1960).
5. H. A. Walter, US Patent No. 2864842 (December 16, 1958); Chem. Abstrs., **53**, 7014d (1959).
6. L. I. Zakharkin, V. V. Gavrilenko, and L. L. Ivanov, Izv. Akad. Nauk SSSR, Ser. Khim., 2067 (1964).