Chemistry

L. Almashi, I. Felmeri, and A. Gants

1958

SovietRxiv

Abstract

Full Text

Chemistry

L. Almashi, I. Felmeri, and A. Gants

Preparation of Halomethyl Derivatives of Aluminum by the Diazoaliphatic Method

(Presented by Academician A. N. Nesmeyanov, 22 XI 1957)

It is known from the literature ($^{1-8}$) that aliphatic diazo compounds can be successfully used for the synthesis of organoelement compounds. Systematic studies in this direction include the work of A. Ya. Yakubovich and his coworkers ($^{2-6}$), who, using this method, developed a procedure for obtaining organic compounds of elements of Groups IV and V of the periodic system.

Organic compounds of elements of Group III of the periodic system, obtained by the diazoaliphatic method, are known only for thallium (^{9}) and for boron (^{10}).

It is of interest to extend this method to the preparation of halomethyl derivatives of aluminum—substances not described in the literature.

In the present work the action of diazomethane on aluminum fluoride, chloride, and bromide was studied.

Considering that the action of diazomethane on boron and thallium halides gave fluoromethyl-difluoroboron and chloro-di-(chloromethyl)thallium, we could expect that in the case of aluminum mono- or di-(halomethyl) derivatives would also be formed. However, these derivatives were not detected even when diazomethane and aluminum halide were taken in a ratio of 1 : 3.

In all cases we obtained only tri-(halomethyl)-aluminum. The reaction apparently proceeded according to the scheme:

$$\mathrm{AlX_3 + 3CH_2N_2 \rightarrow Al(CH_2X)_3 + 3N_2},$$

where $X = \mathrm{Cl, Br}$.

Alkylation of all halogen atoms of an element halide in these reactions is known both for arsenic and antimony (when tri-(haloalkyl) derivatives are obtained) and for tin (when tetra-(haloalkyl) derivatives are obtained). But in all these cases a mixture of all possible derivatives was found, i.e., mono-, di-, tri-, and tetra-(haloalkyl) derivatives, the formation of which is determined by the ratio of the amounts of the aliphatic diazo compound and the halide of the corresponding element. In the case of aluminum we obtained only tri-(halomethyl) derivatives, regardless of the amounts of the starting compounds taken in the reaction.

Aluminum chloride and bromide reacted vigorously with diazomethane even at a temperature of −50°, in contrast to aluminum fluoride, which did not enter into reaction even at room temperature. When "copper bronze" was added to the reaction mixture as a catalyst, decomposition of diazomethane occurred. The only product was "polymethylene," since aluminum fluoride was recovered from the reaction unchanged.

Since the action of diazomethane on element halides consists in the insertion of the biradical "alkylene" between the atoms of halogen and the element, the rate of this reaction depends, under identical conditions, also on the energy

bonds *E*—*X*. Thus, the reaction proceeds more readily when *X* is chlorine or bromine, and with greater difficulty when *X* is fluorine.

Tri-(chloromethyl)aluminum and tri-(bromomethyl)aluminum are crystalline substances, fuming strongly in air and very hygroscopic. They are readily oxidized, and therefore all operations for their preparation were carried out in a stream of dry nitrogen purified of oxygen. These substances are unstable—especially the bromo derivative (even when sealed in a stream of nitrogen, after several days it darkens and decomposes); they are readily soluble in ether in the cold and less soluble in benzene. With water in the cold they react vigorously and decompose, forming hydrogen chloride or, respectively, hydrogen bromide, aluminum hydroxide, and methyl alcohol. All these substances were identified by means of the characteristic generally known qualitative analytical reactions for them.

In the synthesis we used an ethereal solution of diazomethane, obtained by freezing over KOH at −70° and then standing over sodium wire. The amount of diazomethane was determined by titration.

Table 1

Experiment No.	CH_2N_2, g	$AlCl_3$, g	$AlBr_3$, g	$Al(CH_2Cl)_3$, g	$Al(CH_2Cl)_3$, %	$Al(CH_2Br)_3$, g	$Al(CH_2Br)_3$, %
1	3	9.4	19.0				
2	3	3.1	6.3	3.0	72.0	2.7	36.9

The aluminum chloride and bromide used in the reaction were also anhydrous. The reaction was carried out by two methods. To an ethereal solution of diazomethane cooled to −50°, aluminum chloride or, respectively, bromide was added in three portions. A vigorous reaction occurred, the temperature of the solution rose to +10°, and the solution became colorless. The second method differed from the first in that the cooled ethereal solution of diazomethane was added dropwise to a solution of the aluminum halide in ether at −50° over approximately one hour, with stirring. In both cases one and the same product was obtained—tri-(chloromethyl)aluminum, respectively tri-(bromomethyl)aluminum—with approximately the same yields.

After filtering the solution* from the excess aluminum halide and removing the solvent in vacuo in a stream of nitrogen, the residue was subjected to vacuum distillation using a trap cooled to −70°, in order to collect possible lower fractions. As a result of the distillation, a slightly yellowish liquid substance was obtained, which quickly crystallized in the receiver and was the pure product.

Table 2

Substance	B.p., °C/mm Hg	M.p., °C	C, % found	C, % calc.	H, % found	H, % calc.	Al, % found	Al, % calc.	Halogen, % found	Halogen, % calc.
$Al(CH_2Cl)_3$	108–109/1.5	32–33	20.54	20.84	3.45	3.64	15.37	15.15	60.64	60.26
$Al(CH_2Cl)_3$	128–129/4.5	32–33		20.91		3.83		14.84		59.75
$Al(CH_2Br)_3$	119–120/0.7	47–48	11.67	11.52	1.96	1.64	8.73	8.43	77.64	77.44
$Al(CH_2Br)_3$	132–133/2	47–48		12.00		1.86		8.66		76.76

Table 1 gives data on the amounts of starting substances taken in the reaction, as well as the yields of the pure compounds obtained. The yields were calcul- on diazomethane. Table 2 gives the physical constants of the pure substances and the results of their analysis.

Institute of Chemistry, Academy of Sciences
of the Romanian People' s Republic
Cluj Branch

Received
20 XI 1957

---

* The ethereal solution need be filtered only when working by the first method, since under the conditions of this method part of the excess aluminum chloride (and especially bromide) becomes insoluble; it was filtered off at 0–5°.

REFERENCES

[1] L. Hellermann, M. D. Newmann, J. Am. Chem. Soc., **54**, 2859 (1932).
[2] A. Ya. Yakubovich, S. P. Makarov, ZhOKh, **22**, 1528 (1952).
[3] A. Ya. Yakubovich, V. A. Ginsburg, ZhOKh, **22**, 1534 (1952).
[4] A. Ya. Yakubovich, V. A. Ginsburg, ZhOKh, **22**, 1783 (1952).
[5] A. Ya. Yakubovich, S. P. Makarov, G. I. Gavrilov, ZhOKh, **22**, 1788 (1952).

[6] A. Ya. Yakubovich, A. Ya. Merkulova, S. P. Makarov, G. I. Gavrilov, ZhOKh, **22**, 2060 (1952).
[7] D. Seyferth, E. G. Rochow, J. Am. Chem. Soc., **77**, 907 (1955).
[8] D. Seyferth, E. G. Rochow, J. Am. Chem. Soc., **77**, 1302 (1955).
[9] A. Ya. Yakubovich, V. A. Ginsburg, DAN, **73**, 957 (1950).
[10] J. Goubeau, K. H. Rohwedder, Lieb. Ann., **604**, 168 (1957).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.