

energetically with $\text{CHF}_2\text{CH}_2\text{Br}$ or $\text{CHF}_2\text{CH}_2\text{I}$. The reaction was run in ethyl ether, where it still was very vigorous and complete. Instead of acting upon the iodine atom only, the alkali metal removed one atom of fluorine and one atom of iodine, and gave a quantitative yield of sodium fluoride and sodium iodide or bromide. In doing so it behaved like magnesium or zinc.

(4) In contrast with the preceding result, fluorinated derivatives of methane (namely, CCl_2F_2 , CHClF_2 and CHBrF_2) remained unaffected when passed through molten sodium.

THE MIDGLEY FOUNDATION
DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO

RECEIVED MAY 7, 1938

Preparation of Methylaluminum Chlorides

BY VINCENT F. HNIZDA AND CHARLES A. KRAUS

The methyl- and ethylaluminum chlorides have not been reported in the literature until recently. Walker and Willson¹ showed that methyl chloride reacts with aluminum metal when catalyzed by iodine or aluminum chloride, forming an unidentified product which "may be expressed" as $\text{Me}_2\text{-AlCl}$ plus MeAlCl_2 . Hall and Nash² isolated the ethylaluminum chlorides from the products of polymerization of ethylene with a mixture of aluminum and aluminum chloride, and identified the double salt $\text{EtAlCl}_2\cdot\text{NaCl}$. Later, Grosse³ reported the melting and boiling points of the four methyl- and ethylaluminum chlorides.

Since none of these articles gives a satisfactory method of preparation of the compounds in question, it seems desirable to describe briefly the simple method which has been used successfully in these Laboratories since some time prior to the appearance of the articles cited. This description pertains primarily to the methyl chlorides; the ethyl chlorides and the methyl and ethyl bromides have been prepared similarly.

The desired amount of aluminum metal, preferably in an alloy such as Aluminum Company of America Alloy 12 (8% copper), is cut in clean, dry shavings or chips. These are placed in a glass or steel reaction vessel equipped with halide inlet and product discharge lines, temperature and pressure gages, provision for heating and cooling, and a safety blow-out. The catalyst, about 0.1% of anhydrous

aluminum chloride (or iodine, or the product of a previous preparation) is placed in one spot on top of the aluminum, and the reaction vessel closed. Air is pumped or flushed out, and methyl chloride gas introduced to a pressure of one atmosphere (or more, depending on the equipment used). If the reaction fails to start in one hour at room temperature, the charge is heated to 100°. Once started, the reaction is autocatalytic and highly exothermic. More methyl chloride is added, and cooling is applied, at such rates as to maintain a suitable rate of reaction and to keep the temperature of the charge below 75°. At higher temperatures, side reactions may occur with the formation of gas.

When no more methyl chloride is absorbed, the reaction is completed. The reaction of the aluminum is quantitative, while any iron or copper in the alloy remains unattacked. Side reactions are negligible. In a typical preparation, about 60 millimoles of aluminum in the form of alloy took up 88.9 millimoles of methyl chloride with the formation of only 0.9 millimole of methane; the non-volatile residue contained no aluminum and 0.4 milliatom of chlorine; no iron or copper was detected in the distilled product.

The water-white, oily liquid is decanted or vacuum distilled, from the remaining metallic sludge, into a suitable closed container. If desired, this product can be diluted with methyl chloride to lower its viscosity and to facilitate the removal of samples from the container. Such methyl chloride solutions apparently are stable in glass or steel containers, and react slowly with copper or lead. The stability of solutions of the bromides and of the corresponding ethyl compounds is less assured, and is under investigation. In any case, a safety blow-out for the container is recommended. These aluminum compounds are, of course, highly reactive toward air, moisture, and other oxygen compounds; however, their oxidation or inflammation in air is not violent.

The product of the methyl chloride reaction is almost exactly an equimolecular mixture of dimethylaluminum chloride and methylaluminum dichloride. No evidence of either trimethylaluminum or of aluminum chloride is obtained on fractional distillation. Analysis is effected by hydrolysis of a sample with wet ether followed by dilute nitric acid, and determination of the amount of methane evolved, and of the aluminum and chloride content of the solution. In a typical preparation, this analysis gave 13.58 milliatoms of aluminum, 19.60 of chlorine, and 20.46 millimoles of methane, or a ratio of $\text{Me}:\text{Al}:\text{Cl}$ of 1.507:1:1.443.

When the individual compounds are desired, they may be separated from their mixture by fractional vacuum distillation, or the dimethylaluminum chloride may be obtained in pure form by heating the mixture with excess sodium chloride and distilling the dimethyl compound from the mono-methyl addition compound. Analysis of a typical distillate from the latter procedure gave 23.4 milliatoms of aluminum, 23.6 of chlorine, and 47.1 millimoles of methane, or a ratio of $\text{Me}:\text{Al}:\text{Cl}$ of 2.01:1:1.01.

RESEARCH LABORATORIES
ETHYL GASOLINE CORPORATION
DETROIT, MICHIGAN
NEWPORT ROGERS LABORATORY
BROWN UNIVERSITY
PROVIDENCE, R. I.

RECEIVED AUGUST 1, 1938

(1) W. O. Walker and K. S. Willson, *Refrig. Eng.*, **34**, 89, 126 (1937).

(2) F. C. Hall and A. W. Nash, *J. Inst. Petroleum Tech.*, **23**, 679 (1937).

(3) Abstracts, American Chemical Society, Dallas Meeting, 1938.