

METHYLENE BIS(ALUMINUM DIHALIDES)

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SUMMARY

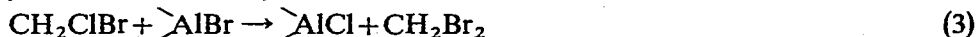
Methylene bis(aluminum dichloride) and methylene bis(aluminum dibromide) have been synthesized in essentially quantitative yields. It is postulated that the reaction sequence which leads to these compounds requires aluminum monohalide as a transitory intermediate.

INTRODUCTION

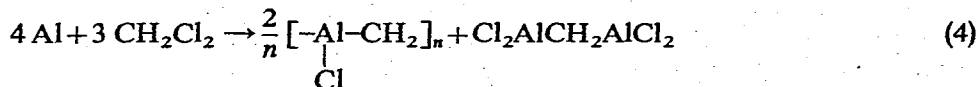
The reaction of aluminum with alkyl halides to give alkylaluminum sesquihalides [eqn. (1)] has been known for over a century.



However, the reaction of aluminum with dihalomethanes has received little attention¹⁻³. Information on the nature of the products from this reaction was first published by Lehmkuhl and Schäfer⁴ in 1966. They reported isolating and characterizing methylene bis(aluminum dichloride) (I) in approximately 40% yield from the reaction of aluminum and dichloromethane initiated by small amounts of dibromomethane or aluminum bromide. The reaction proceeded via a halogen exchange mechanism in which dibromomethane was regenerated according to eqns. (2) and (3).



Lehmkuhl and Schäfer suggested that the reaction of aluminum with dichloromethane was analogous to the reaction of aluminum with alkyl halides [eqn. (4)].



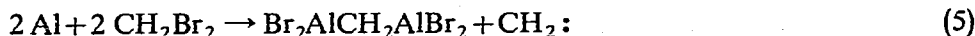
These authors also reported that the direct reaction of dichloromethane and aluminum does not occur. These results have been confirmed by us. We have reported⁵ the synthesis of (I) by an electrochemical-chemical method.

In this paper we report our studies on direct and indirect reactions of aluminum

with dihalomethanes and propose a reaction scheme to account for all the products.

RESULTS AND DISCUSSION

The reaction of aluminum with excess dibromomethane yields methylene bis(aluminum dibromide) (II) according to eqn. (5).

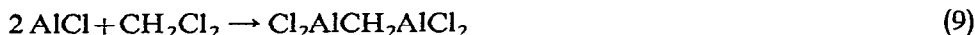


The other products of the reaction were ethylene, cyclopropane, 1,2-dibromoethane, and methyl bromide. With the possible exception of methyl bromide*, these products would result from the reactions of methylene or organoaluminum intermediates involving methylene transfer reactions [eqns. (6)–(8)].



During the reaction, slightly more than one mole of dibromomethane is consumed per g-atom of aluminum. This excess amount of dibromomethane is accounted for as dibromoethane [eqn. (8)]. The conversion of Al to (II) is quantitative.

Based on these results and those from the electrochemical–chemical synthesis of (I)⁵, we suggest that aluminum monohalide is the key intermediate in the reaction sequence leading to (I) or (II). In the electrochemical–chemical synthesis of (I) it was proposed that chloride was oxidized to atomic chlorine which attacked the aluminum anode to produce aluminum monochloride. This transitory intermediate reacted with dichloromethane to give (I) [eqn. (9)].



The cathode reaction in the electrochemical–chemical method was the reduction of dichloromethane.

If, in the reaction of dibromomethane with aluminum, the first step is the reduction of dibromomethane, then aluminum monobromide, methylene and/or a bromomethyl radical would be expected products [eqns. (10) and (11)].



These intermediates can account for all the products found.

The direct reaction of aluminum with dichloromethane does not occur. This is attributed to the failure of aluminum to reduce dichloromethane. If the formation of aluminum monochloride is the necessary initial step then (I) should be obtained if other means are used to produce this intermediate. We have used two methods to produce aluminum monochloride [eqns. (12) and (13)].

* H. D. Roth⁶ has reported that singlet methylene abstracts chlorine from alkyl chlorides to give a chloromethyl radical. The chloromethyl radical then abstracts hydrogen or chlorine to give either methyl chloride or dichloromethane. This reaction would account for all the products we observed as being derived from methylene.



When these reactions are carried out in dichloromethane, (I) is obtained along with other products.

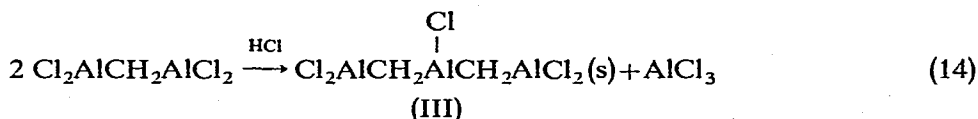
The possibility that HCl removed surface oxide coating to provide a fresh metal surface for reaction with dichloromethane was investigated by using a 1/5 molar ratio of HCl to aluminum. Under these conditions most of the aluminum was recovered unreacted.

Further evidence that reduction of dibromomethane with aluminum leads to products from the reactions of methylene [eqns. (6)–(8)] is provided in the analysis of the by-product gases from the reaction of HCl with aluminum in excess dichloromethane. The gaseous products were methane, hydrogen, and a small amount of methyl chloride. The methylene reaction products, ethylene and cyclopropane were not detected.

The formation of products from the reactions of "methylene" in the reduction step again raises the question whether or not free methylene exists in organometallic reactions⁷. Hoberg⁸ reported that ethylene and cyclopropane were obtained from the reaction of CH_2N_2 with dialkylaluminum halides presumably as decomposition products of $\text{Et}_2\text{Al}(\text{CH}_2)_2\text{Cl}$ and $\text{Et}_2\text{Al}(\text{CH}_2)_3\text{Cl}$. The formation and decomposition of $\text{Br}_2\text{Al}(\text{CH}_2)_2\text{Br}$ and $\text{Br}_2\text{Al}(\text{CH}_2)_3\text{Br}$ to give ethylene, cyclopropane, and AlBr_3 are not consistent with the products and stoichiometry of the reaction of aluminum and dibromomethane.

Hoberg's mechanism can be applied only to $\text{>Al}(\text{CH}_2)_2\text{Br}$ and $\text{>Al}(\text{CH}_2)_3\text{Br}$ where the aluminum still has metal to metal bonds. The latter intermediates are the products of methylene insertion in the Al–C bonds by free methylene or by methylene transfer reactions. The 1,2-dibromomethane* would result from a competitive reaction of methylene with the large excess of dibromomethane.

Under certain conditions a higher molecular weight product was formed in addition to (I). The purity of the aluminum, the dryness of the dihalomethane and the use of excess dihalomethane were major factors in determining the composition of the products from the reaction. If traces of moisture or HCl are present, higher molecular weight products are produced. We have found that traces of anhydrous HCl catalyze the exchange reaction of (I) [eqn. (14)].



The dihalomethane can be dried sufficiently to avoid by-product formation by the use of molecular sieves; P_2O_5 and CaH_2 were not effective.

Solutions of (I) in CH_2Cl_2 are stable for over a year in the absence of HCl or traces of water. This is true for solutions of (I) prepared by the exchange of chloride

* A referee suggested the 1,2-dibromomethane might result from Wurtz type reactions. However, aluminum is not one of the metals associated with Wurtz reactions. The reaction of aluminum with alkyl halides to give alkylaluminum halides has been well documented.

for bromide [eqn. (15)] and for solutions of (I) prepared by the electrochemical-chemical method in which solutions of (I) are used as the electrolyte.



When (I) is prepared under our best conditions and converted to the dietherate, only a singlet at τ 11.14 is observed in the NMR spectrum⁵. Likewise, no products are produced which are insoluble in CH_2Cl_2 . The singlet in the NMR spectrum assigned to (III) trietherate (τ 10.44) only appears when products insoluble in CH_2Cl_2 are present.

The addition of a small amount of anhydrous HCl or water to a solution of (I) results in the formation of (III). Likewise, when HCl is used to produce (I), (III) is always present in the reaction mixture.

We do not believe the exchange reaction [eqn. (15)] produces a higher mol.wt. product than (III). A product of higher mol.wt. should give a peak in the NMR shifted from the singlet assigned to (III) trietherate. This has not been observed. Since (III) is insoluble in CH_2Cl_2 , the chances of further exchange reactions occurring seem unlikely.

The reaction conditions used by Lehmkuhl and Schäfer were not reported. Shearer and Coover³ reported that the reaction of dibromomethane with excess aluminum (3/4 mole ratio) gave a polymeric reaction product whose structure was not readily definable. If Lehmkuhl and Schäfer used an excess of aluminum in their synthesis the polymeric product might be explained. The formation of (I) could have resulted in the extraction process where excess dichloromethane was used.

EXPERIMENTAL

Properties

(I) and (II) are solids which do not melt without decomposition. They are insoluble in aliphatic hydrocarbons and are sparingly soluble in benzene. Cryoscopic mol.wt. determination in benzene showed both (I) and (II) to be trimeric.

The proton NMR spectrum for (I) and (III) etherates were previously reported⁵. The proton NMR spectrum for (II) dietherate shows a singlet for the alCH_2al protons at τ 10.73, a triplet for the CH_3 protons of Et_2O at τ 8.57 and a quartet for the CH_2 protons of Et_2O at τ 5.77 (TMS reference) ratio 1.7/12/8.3. The proton-NMR spectrum for (I) in dichloromethane shows a singlet at τ 10.34.

(I) and (II) are not pyrophoric and do not appear to react with air. A slurry of (II) in CH_2Br_2 was stirred under dry air pressure (50 mmHg) for 8 h at room temperature. Samples were removed at 0, 1, 3 and 8 h and converted to the dietherate. The proton NMR spectra of these samples were identical. The fact that (I) and (II) do not react with oxygen has permitted us to study the effect of oxygen in olefin polymerization where only part of the catalyst is oxygen-sensitive.

Apparatus

Standard laboratory glassware was thoroughly cleaned and dried in an air-circulating oven at 140° , assembled hot and cooled under dry nitrogen.

Materials

Aluminum 99.99% pure was obtained in sheet form from Consolidated Alumi-

num Co. of Canada. Dibromomethane (Eastman 1903) and dichloromethane (Fisher Scientific D37) were dried by passage through a 3' x 1" column packed with Linde 3A molecular sieves.

Methods

All transfers and reactions were carried out under Airco prepurified nitrogen. All liquid transfers were made with hypodermic syringes. NMR spectra were obtained on either Varian A-60 or A-56-60 spectrometers. The internal standards were either TMS or the dihalomethane. Where the dihalomethane was used as the internal standard, the values were converted to TMS reference for comparison.

The mass spectroscopy data were obtained with a CEC 103 mass spectrometer.

Methylene bis(aluminum dibromide)

Aluminum, 62 mg atom, (in about 3 mm squares) was stirred in 87.5 g of dibromomethane. The reaction usually commenced in about 15 min or the induction period was shortened by briefly heating the mixture. The exothermic reaction continued until all of the aluminum reacted and was controlled by cooling. A clear homogeneous light amber colored solution was obtained. On standing, a fine precipitate of (II) was obtained. The excess dibromomethane (76.5 g) was recovered by distillation. The remaining 11.0 g (6.33 mmol) of dibromomethane was consumed in the reaction. The yield of (II) was 12.4 g (100% based on aluminum).

During the course of the reaction a sample of the by-product off-gases was obtained and analyzed by mass spectroscopy. The following analysis was obtained (mole %): C₂H₄ 55.30, C₃H₆ 31.20, CH₃Br 9.40, C₂H₃Br 1.63, C₆H₁₂ 1.87 and C₄H₈ 0.43. The C₃H₆ was identified as cyclopropane by comparing the GLC retention time with known samples of cyclopropane and propylene using a 3 m Poropak Q column at 100°.

The recovered dibromomethane was analyzed by GLC-rapid scan mass spectroscopy and found to be 98.3% dibromomethane and 1.7% 1,2-dibromoethane. The starting dibromomethane was shown to be 100% pure by GLC. The methylene bis(aluminum dibromide) was analyzed for Br⁻, Al, and Al-C bonds. The aluminum carbon bonds were analyzed by the method of Bartekiewicz and Robinson⁹ except the solvent for the iodine was dichloromethane instead of benzene. The Br⁻ and Al-C bonds were determined on the CH₂(AlBr₂)₂ in dibromomethane. (Found: Br⁻/Al, 2.03, 2.04; Al-C bonds/Al, 1.08, 1.02; Al, 13.63, 13.68; mol.wt. cryoscopic in benzene, 1126. CH₂Al₂Br₄ calcd.: Br⁻/Al, 2.00; Al-C bonds/Al, 1.00; Al, 13.92%, mol.wt. (trimer), 1163.)

Methylene bis(aluminum dichloride)

Halogen exchange. Aluminum, 60 mg atom, (in about 3 mm squares) was stirred in a mixture of 50 ml of dichloromethane and 1.5 ml of dibromomethane. The mixture was refluxed for 20 h during which time all of the aluminum reacted. A homogeneous, stable solution was obtained. The excess dichloromethane was removed by distillation. The yield of (I) was 6.3 g (100% based on aluminium). Found: mol.wt. cryoscopic in benzene, 629. CH₂Al₂Cl₄ calcd.: mol.wt. (trimer), 629.

HCl as an initiator

(i). To a solution of 5.7 mmol of HCl in dichloromethane was added 5.7 mg

atom of aluminum (in about 3 mm squares). The mixture was stirred for 20 h during which time all the aluminum reacted. The product was a slurry of a white solid product. The entire product was converted to the etherate. The NMR spectrum showed the characteristic peaks at τ 11.14 and 10.44 for (II) and (III) respectively.

The by-product off-gases were collected from a similar experiment and analyzed by mass spectroscopy. The following analyses were obtained in mole %: CH_4 89.9%, H_2 8.4%, and CH_3Cl 1.6%.

(ii). To a solution of 21 mmol of HCl in dichloromethane was added 0.10 g atom of aluminum (in about 3 mm squares). The mixture was stirred for 5 days and contained unreacted aluminum. The reaction mixture was decomposed with methanol and the unreacted aluminum (61 mg atom) was recovered. The mole ratio of aluminum reacted per HCl was 1.85.

Cl₂ as an initiator

To a solution of 16 mmol of chlorine in dichloromethane in a black flask to exclude light was added 34 mg atom of aluminum (in about 3 mm squares). After stirring for 2 days part of the aluminum remained unreacted. The product slurry was converted to the etherate. The NMR spectrum showed the characteristic peaks at τ 11.18 and 10.53 for (I) and (III), respectively. The unreacted aluminum (12.5 mg atom) was recovered showing that 21.4 mg atom of aluminum had reacted. The failure to obtain complete reaction indicates either some AlCl_3 was formed or some chlorination of the dichloromethane occurred.

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