A STUDY OF THE COMPOSITION AND SOME REACTIONS OF THE ETHERATE OF ALUMINUM TRIETHYL

DISSERTATION

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A STUDY OF THE COMPOSITION AND SOME REACTIONS OF THE ETHERATE OF ALUMINUM TRIETHYL

CHAPTER I. INTRODUCTION

A. Purpose and Scope of this Research

Aluminum triethyl was first prepared in 1865 by Buckton and Odling[1] and its etherate fifty-eight years later by Krause and Wendt[2]. Thus these compounds have been in the chemical literature for many years, but their chemical reactions have been relatively little studied, chiefly because of the difficulty of their preparation and because their reactivity makes them hard to handle. Aluminum triethyl, like the trimethyl, is dimerized and interest in this motivated physical measurements leading to the determination of its structure and caused considerable discussion concerning the type of bonding involved in formation of the dimers [3 through 16]. Some work has been done with the reactions of aluminum triethyl and its etherate with organic compounds. With chloral, bromal, monochloroacetone, trichloroacetone and trichloracetophenone, aluminum triethyl etherate was found to behave as a reducing agent, giving good yields of the corresponding primary alcohol and ethylene. With benzaldehyde, p-chlorbenzaldehyde, anisaldehyde and cinnamic aldehyde, a secondary alcohol, the corresponding aryl-ethyl carbinol, was obtained as the principal product[17]. Phenyl isocyanate and aluminum triethyl gave a 27% yield of propio-anilide[18]. Dibenzofuran did not react with aluminum triethyl; it was not metallated even at high temperatures[19].

However, no work has been done on the reactions of aluminum triethyl or its etherate with inorganic compounds, except for the observation of Buckton and Odling that aluminum triethyl reacts with iodine to form iodine-containing derivatives and ethyl iodide, and that it absorbs oxygen from dry air[1]. It was decided, therefore, to study the reactions of aluminum triethyl etherate with some simple inorganic compounds and with some Lewis bases.

In the course of this work it was thought desirable to determine the composition of the etherate, since Krause and Wendt[2] gave its empirical formula, after analysis, as $4\ Al(C_2H_5)_3 \cdot 3\ (C_2H_5)_2O$, and this formula seemed improbable. The formula $Al(C_2H_5)_3 \cdot (C_2H_5)_2O$ is more logical since it may be interpreted by assuming that each of the aluminum atoms accepts an electron-pair from the oxygen atom of a diethyl ether molecule. It was decided to investigate the freezing point-composition curve of the system aluminum triethyl-diethyl ether. This phase study should show all existing etherates and give the compositions of those that melt congruently.

B. Review of Methods of Preparation of Aluminum Triethyl and its Etherate.

Aluminum Triethyl. The compound was first prepared by Buckton and Odling[1] from mercury diethyl and aluminum. Excess aluminum, in the form of chips or foil, is used, and it and the mercury diethyl are placed in a bomb tube. The glass tube is sealed and heated for thirty hours at 100-120°C. The aluminum triethyl is purified by distillation from fresh aluminum. This method has the disadvantage that the reaction is carried out in a sealed tube, and it requires the use of the extremely toxic mercury diethyl. Buckton and Odling[1] did not give the yield obtained but stated only that aluminum triethyl was obtained in not unimportant amount. Krause and Wendt[2] did not get an "outstanding yield" and found that a considerable amount of hydrocarbons was formed. When the heating period was shortened, much mercury diethyl remained unreacted. Other workers[20] found that aluminum triethyl prepared by this method boiled over an eleven-degree range and contained mercury diethyl as an impurity. Later, Bamford, Levi, and Newitt[13] obtained aluminum triethyl in almost theoretical yield by this method.

An alternate method of preparation is that given by Grosse and Mavity[21] involving the reaction of an aluminum-magnesium alloy with ether-free ethyl bromide, followed by treatment of the resulting mixture of aluminum ethyl bromides with sodium. A modification of Grosse and Mavity's method was employed for obtaining the aluminum triethyl used in this research.

Aluminum Triethyl Etherate. The etherate may be obtained by adding diethyl ether to aluminum triethyl[2]. It has also been prepared by the reaction of an ether solution of ethyl bromide with an aluminum-magnesium alloy[2]. A third method involves the reaction of anhydrous aluminum chloride with excess ethyl magnesium bromide in ether solution[2]. The last method was used to prepare the etherate for this research and was found to be quite reliable.

C. Properties Given in the Literature.

Aluminum Triethyl. Aluminum triethyl is a clear, water-white liquid at room temperature, more viscous than water. The boiling point is given variously as 194°C.[1], 185.6°C.[6], and 207.0°C.[13]. The melting point is recorded as -52.5°C.[14]. The compound is about 12% associated to the dimer at 150.6°C.[14]. If it is heated above 165°C. for long periods it undergoes decomposition[14]. It has low volatility and distils extremely slowly in a vacuum.

Chemically, this material is quite reactive, igniting spontaneously in air and burning with a yellow sooty flame. It reacts with water with explosive violence.

Aluminum Triethyl Etherate. Aluminum triethyl etherate differs little in appearance and chemical properties from aluminum triethyl. It boils at 216-18°C. with very little decomposition or loss of ether. Its density is given as 0.8200 g./cc. Krause and Wendt state that by analysis the composition of the etherate is $4\ Al(C_2H_5)_3 \cdot 3\ (C_2H_5)_2O$ [2]. Its melting point has not been recorded in the literature.

It fumes immediately and vigorously in air, giving a smoke of a finely divided white powder and a peculiar odor. The liquid becomes quite hot in air and occasionally ignites. It chars cotton fiber or wood.

CHAPTER II. EXPERIMENTAL RESULTS AND DISCUSSION

A. Experimental Methods and Precautions Employed in This Work.

Because of the extremely reactive nature of the materials used in this research special techniques were necessary for their handling. With few exceptions the materials must be prepared, purified, stored and sampled under a dry, inert atmosphere. General precautions and methods are given below; more specific techniques will be described in the various procedures for the individual experiments.

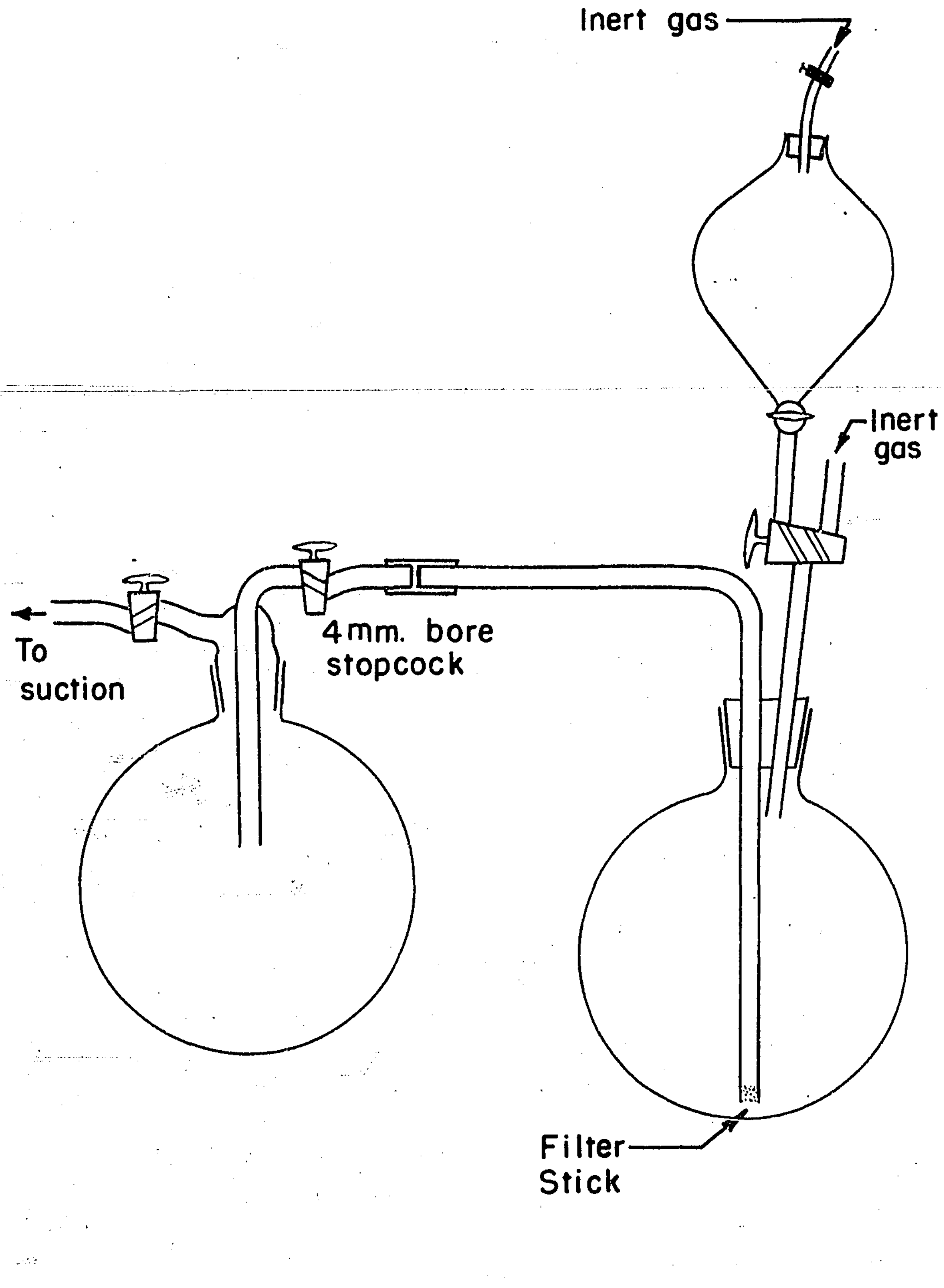
Mercury diethyl is a deadly substance. One of the early workers with mercury dialkyls, Frankland, lost two laboratory assistants by death and insanity through the careless handling of these compounds[22]. It must always be used in a good hood and great care taken to avoid spilling the material on wooden floors or desks from which it can slowly volatilize.

Aluminum triethyl, its etherate, the alkali metal alkyls, and many of their reaction products react violently with water and inflame spontaneously in air. They react with cork, rubber, and organic stopcock grease. Even Silicone high-vacuum grease was attacked, but it was used sparingly when necessary. The reaction with mercury, (if any) was slow and a mercury-seal stirrer was used in preparing these compounds. All equipment was thoroughly dried, usually overnight in an oven at 120°C. All solvents were dried, usually over sodium wire, and outgassed with dry nitrogen.

It was not possible to make transfers by pouring from one vessel to another, since even this short exposure to the air results in considerable hydrolysis and even fire. Transfers were effected by use of pressure or vacuum to force the liquid through glass tubing, or in the case of dilute solutions, through Tygon tubing. Sometimes a pipet, previously swept with nitrogen, was filled, in a nitrogen atmosphere, by suction or pressure. Whenever possible the compounds were vacuum distilled directly into the flask in which they were to be used. This procedure was followed in instances where the highest purity was desired, as in the phase studies.

Inverse filtration was used in all cases (Fig. 1). A slightly greater-than-atmospheric pressure of inert gas was maintained in the flask in which the filter stick was inserted. The filter stick was connected to a receiver on which suction was applied.

Residues from preparations often contained sodium or lithium metal and aluminum triethyl. They were particularly troublesome to dispose of and in spite of all precautions fires often resulted during their destruction. The most satisfactory method found was to place the flask in a hood behind a safety shield and remove all stoppers, allowing free access to the air. After several hours alcohol was added slowly with care, and then, in turn, water and acid, stirring the solid residue after each addition. This process could not be safely hurried; several hours were often required.



APPARATUS FOR FILTRATION

FIGURE I

Nitrogen was used as an inert atmosphere in all work except in the preparation of the lithium ethyl, where helium was required. Both gases were purified by passing through (a) two gas-washing bottles of Fieser's solution[23] to remove oxygen, (b) one gas-washing bottle of saturated lead acetate solution to remove traces of hydrogen sulfide from the Fieser's solution, (c) two gas-washing bottles (with fritted-glass dispersion discs) containing fresh concentrated sulfuric acid, (d) one tower filled with Ascarite and Drierite, and (e) one tower filled with a mixture of phosphoric anhydride and sand.

B. Preparation of Aluminum Triethyl and Its Etherate.

Aluminum Triethyl. The following procedure was used for the preparation of aluminum triethyl; it is an adaptation of that of Grosse and Mavity[21]. The process is represented essentially by the equations:

$$2Al + 3C_2H_5Br \longrightarrow Al(C_2H_5)_2Br + Al(C_2H_5)Br_2$$

$$Al(C_2H_5)_2Br + Al(C_2H_5)Br_2 + 3Na \longrightarrow Al(C_2H_5)_3 + 3NaBr + Al$$

A 1000 ml. three-neck flask equipped with a condenser, pressure-equalizing dropping funnel, and mercury-seal Hershberg stirrer was used. A stream of nitrogen was kept running through the apparatus during all operations. Fifty-four grams of granular aluminum (20 mesh), a few tenths of a gram of finely powdered aluminum, and a crystal of iodine were added to the reaction flask. After the apparatus was flushed with nitrogen, 250 ml. of ether-free ethyl bromide was added to the dropping funnel. After further sweeping with nitrogen, enough ethyl bromide was run into the reaction flask to cover the aluminum. Stirring was started and ethyl bromide was added, slowly. After about an hour a vigorous reaction began. In some of the runs, it was necessary to initiate the reaction by heating until the ethyl bromide refluxed. Addition of ethyl bromide was stopped until the reaction had subsided somewhat. Dropwise addition was then resumed and continued until all ethyl bromide had been added. The reaction mixture was then heated for three to six hours. There was very little refluxing although the temperature of the reaction flask became too high to touch. The flask was cooled below the melting point of sodium and a total of 72 g. of sodium, in 5 to 15 g. lots, was added. The small pieces of sodium were added through the condenser in a countercurrent of nitrogen. After a lot (5 to 15 g.) of sodium had been added, the reaction mixture was heated, with stirring, to a temperature above the melting point of sodium. As the molten sodium was stirred through the liquid, a highly exothermic reaction took place, which caused vigorous refluxing. After the reaction quieted, the flask was cooled and another lot of sodium added. It was then heated again until reaction took place. This procedure was repeated until all 72 g. of sodium had been added. When almost all of the sodium had been added, the flask became so full of black-gray solid that stirring became impossible. The flask was heated for about one hour, then the stirrer was removed. The few pieces of material clinging to the stirrer immediately burst into yellow flames as they were exposed to the air. A Claisen head was fitted into the reaction flask and this in turn was attached to a Friedrichs condenser. A three-neck flask served as a receiver. The black-gray mass was subjected to vacuum distillation. The boiling point of the distillate was 76°C. at 2.5 mm., 69°C. at 1.5 mm.

The product was a colorless, clear liquid. When a sample of it was hydrolyzed, acidified, and tested with silver nitrate solution, it gave no perceptible precipitate. The most likely impurities are hydrocarbons from pyrolysis of the aluminum alkyl halides or aluminum triethyl.

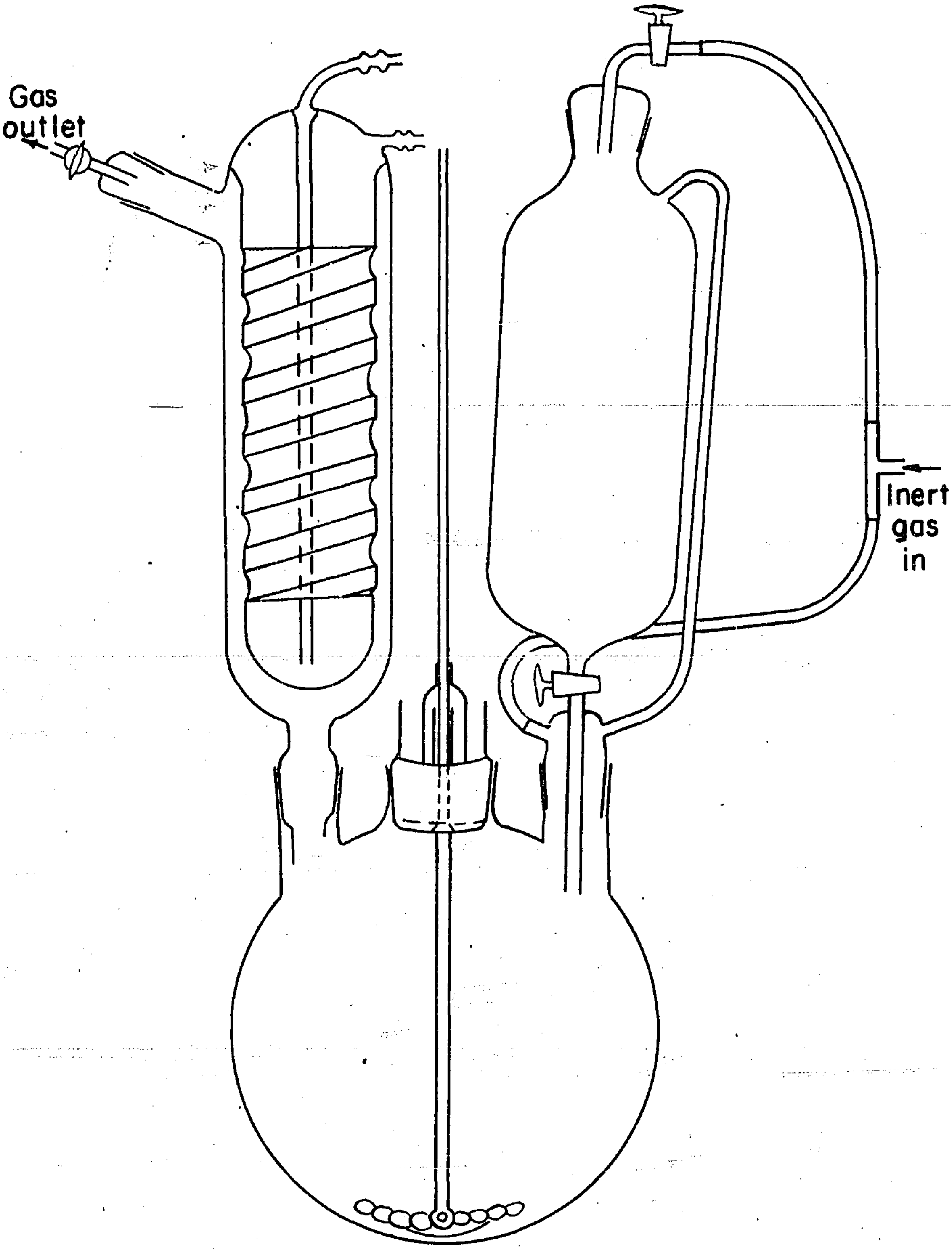
This procedure was carried through five times and was successful three of the five. In the unsuccessful runs considerable distillate was obtained but it seemed to be lower boiling than aluminum triethyl and it contained large quantities of bromides. No reason is known for the failure of two preparations. However, in these cases the sodium was added in a smaller number of lots (more than 15 g. in a lot) and also the individual pieces of sodium may have been larger, so perhaps reaction with the sodium was not complete.

<u>Aluminum Triethyl Etherate</u>. The procedure used followed in general those of Krause and Wendt[2] and Hurd[24]. Ethyl magnesium bromide was prepared in the usual manner by dropwise addition of 136 ml. of ethyl bromide, dissolved in 200 ml. of ether, to 39 grams of magnesium covered with 300 ml. of ether. The preparation was carried

out in a 2-liter, 3-neck flask equipped with a pressure-equalizing dropping funnel, mercury-seal stirrer, condenser, and inlet and outlet for nitrogen (Fig. 2). After all of the ethyl bromide was added, the Grignard reagent was refluxed for one hour and then 43 grams of anhydrous aluminum chloride, dissolved in 500 ml. of ether, was added dropwise with vigorous stirring. The mixture was refluxed with continuous stirring for two hours. The stirrer was removed. The ether was distilled off; the solid gray-white residue which remained subjected to vacuum distillation, and the distillate collected in a 250-ml. flask which had been weighed together with stoppers. In a typical run a yield of 45 g. of the etherate (74% of theory) was obtained. A sample was hydrolyzed, acidified with nitric acid, and silver nitrate solution was added; no precipitate resulted.

C. A Phase Study of The Binary System Aluminum Triethyl-Diethyl Ether.

Discussion. Krause and Wendt first reported the preparation of aluminum triethyl etherate[2], which they analyzed, and on the basis of their analysis assigned to it the formula $4Al(C_2H_5)_3.3(C_2H_5)_2O$. Krause and Grosse[25] and Sidgwick[26] have suggested that this formula is incorrect and that the compound is $Al(C_2H_5)_3.(C_2H_5)_2O$. This latter formula is more reasonable particularly since monomeric 1:1 addition compounds of aluminum trimethyl with dimethyl ether, trimethylamine, trimethylphosphine and dimethyl sulfide are known[27]. Also the Raman spectra of aluminum trimethyl etherate[3]



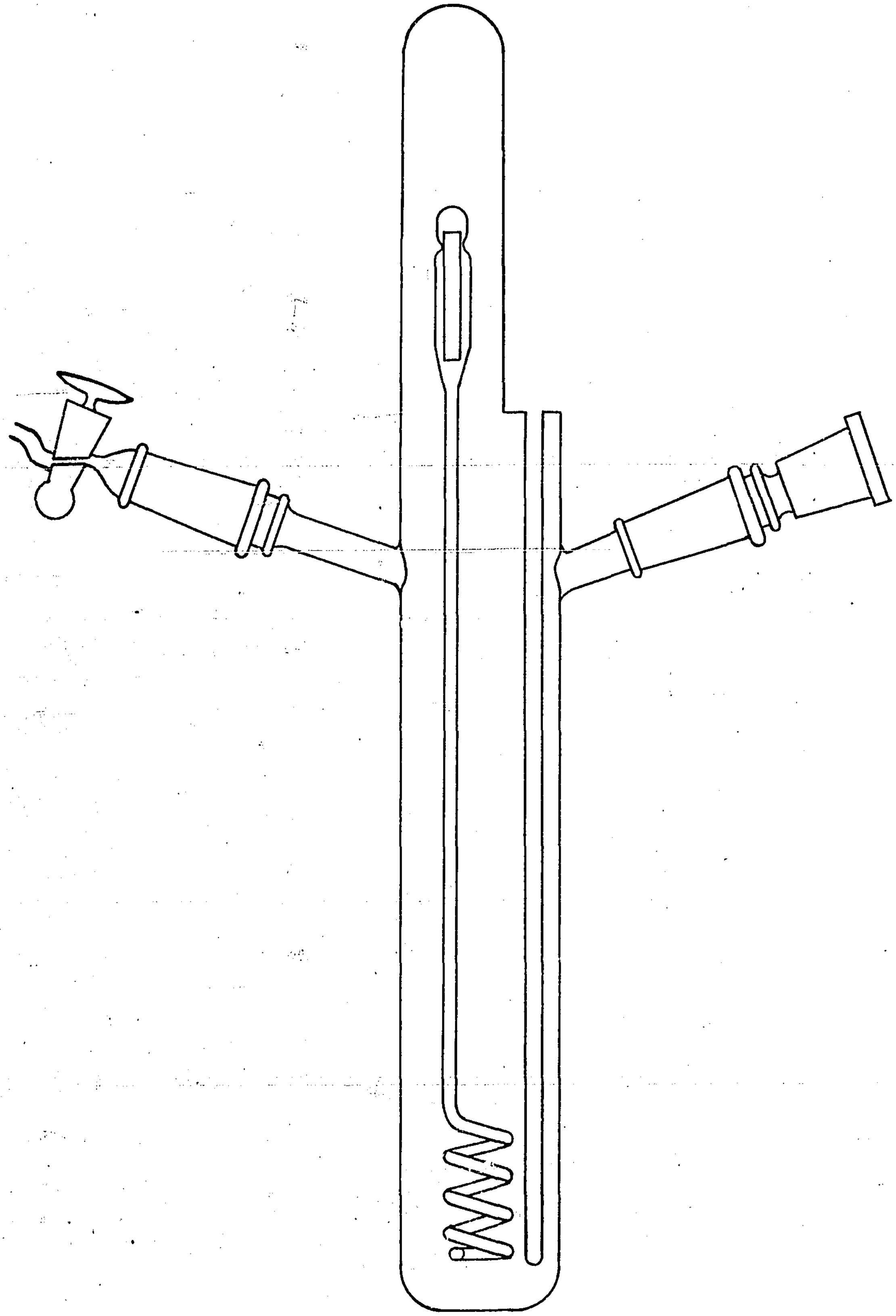
APPARATUS FOR PREPARATION OF ALUMINUM TRIETHYL ETHERATE
FIGURE 2

show that this compound is a molecular compound in which diethyl ether and the aluminum trimethyl are closely linked. In order to settle the question of whether the etherate is $4Al(C_2H_5)_3 \cdot 3(C_2H_5)_2O$ or $Al(C_2H_5)_3 \cdot (C_2H_5)_2O$, or whether both are formed, it was decided to determine the freezing point-composition diagram.

Purification of Materials. Aluminum triethyl was prepared as described above. It was distilled under vacuum from the receiver into the freezing-point cell. Difficulty was encountered in obtaining the freezing point of the aluminum triethyl since it had a great tendency to supercool and since even a small amount of supercooling seemed to make the freezing point low. Pitzer and Gutowsky obtained a melting point of -52.5°C. using a pentane thermometer calibrated by the Bureau of Standards and a Dry Ice bath[14]. The freezing points obtained in this study, using a copper-constantan thermocouple attached to a Leeds and Northrup Micromax self-recording potentiometer, were -50.3°C. and -50.7°C.

Anhydrous reagent grade diethyl ether (J.T. Baker Chemical Co.) was dried over sodium wire and iron wire and copper powder were added to minimize peroxide formation. The ether was outgassed with nitrogen. The freezing point, taken using a previously calibrated apparatus, was -123.5°C. The literature value for the β form is -123.3°C.

Experimental Procedure. The freezing points of the various mixtures of aluminum triethyl and diethyl ether was determined in an enclosed all-glass cell equipped with two ground-glass inlets(Fig.3).



FREEZING POINT CELL

FIGURE 3

The cell contained a stirrer consisting of a glass spiral with a glass-enclosed iron slug at the upper end. Stirring was effected when an intermittent current was applied to an air-cooled solenoid placed around the neck of the freezing-point cell. A thermocouple well was built into the cell.

After the aluminum triethyl had been distilled (under vacuum) into the freezing-point cell, nitrogen was admitted to the apparatus until it was at slightly greater than atmospheric pressure. Then the cell was removed and stoppered quickly with a ground-glass joint fitted with a large serum-bottle stopper. The weight of aluminum triethyl was determined by weighing the freezing-point cell before and after the distillation. Additions of ether were made by using a syringe equipped with a one and one-half inch, twenty-six gauge needle. The quality of the serum-bottle stoppers seemed to vary widely; some did not leak after twenty punctures, but some leaked after only one. The freezing-point cell was weighed before and after each ether addition in order to determine the amount of ether added. Before the cell was weighed, all the heat-transfer liquid (30-60°C. fraction, petroleum ether) was removed with pipe-cleaners. In this way any change in weight due to leakage was detectable. The cell was cooled in Dry Ice-acetone before an ether addition was made.

When freezing points were taken, cooling of the cell was controlled by varying the cooling bath, either liquid nitrogen or a mixture of Dry Ice and acetone, or by varying the jacket in which the cell was placed. These jackets consisted of a single glass tube, or a pair of insulated concentric glass tubes, or two tubes joined together at the top and equipped with a stopcock so that the space between the tubes could be evacuated to any desired pressure. The jackets also varied in diameter. The cooling bath and jacket were chosen so as to give the slowest cooling rate practicable, usually between 0.5°C./min. and 2°C./min.

Temperatures were measured with a recording potentiometer (Leeds and Northrup Micromax) using a copper-constantan thermocouple immersed in the well of the freezing-point cell. The heat-transfer medium in the well was petroleum ether, 30-60°C. fraction. The apparatus was calibrated at the freezing points of distilled water, chloroform, carbon tetrachloride and diethyl ether. While the method is capable of accuracy within ± 1.5°, the extreme reactivity of aluminum triethyl and consequent difficulty in obtaining and keeping it pure, the apparently low heats of fusion which make it difficult to obtain sharp changes of slope, and the tendency of the mixtures to supercool make the freezing points obtained from zero to eighty mole per cent ether probably not better than ± 2°. From eighty mole per cent to one hundred mole per cent it was necessary to determine most of the freezing points visually, as the formation of a solid did not affect the slope of the time-temperature curve enough to be detected. This method increases the uncertainty of these points. Also, in this region of higher ether percentages, several samples had to be discarded because they showed weight losses.

Supercooling was frequently encountered. Tiny pieces of platinum wire placed inside the cell seemed to help to prevent it, as did scratches (from much stirring) on the inside of the cell. Often it was necessary to freeze the mixture with liquid nitrogen, warm it with the hands, and then when most of the solid had liquefied and the temperature was near the freezing point, the cell was immersed in the cooled jacket. The few remaining crystals acted as nuclei for further crystallization and the freezing point of the mixture was then obtained.

Because some ambiguity was encountered in interpreting the results of the freezing point curve, it was decided to prepare a pure sample of the etherate, determine its freezing point and the effect of ether addition on that freezing point and to analyze it for aluminum. The freezing points on the aluminum triethyl etherate were obtained in the same manner as above, the etherate being distilled directly into the cell. Samples of etherate from two different preparations were used. Weighed portions of ether were added and the freezing points of the mixtures determined. The same sample on which the freezing points were obtained was carefully hydrolyzed, and analyzed for aluminum. The aluminum was precipitated and weighed as 8-hydroxyquinolate[28].

Results. The data obtained for the system aluminum triethyl-diethyl ether are listed in Table I and shown graphically in Figure 4. The formation of a compound between aluminum triethyl and diethyl ether is indicated by the maximum in the curve at about -65°C. and

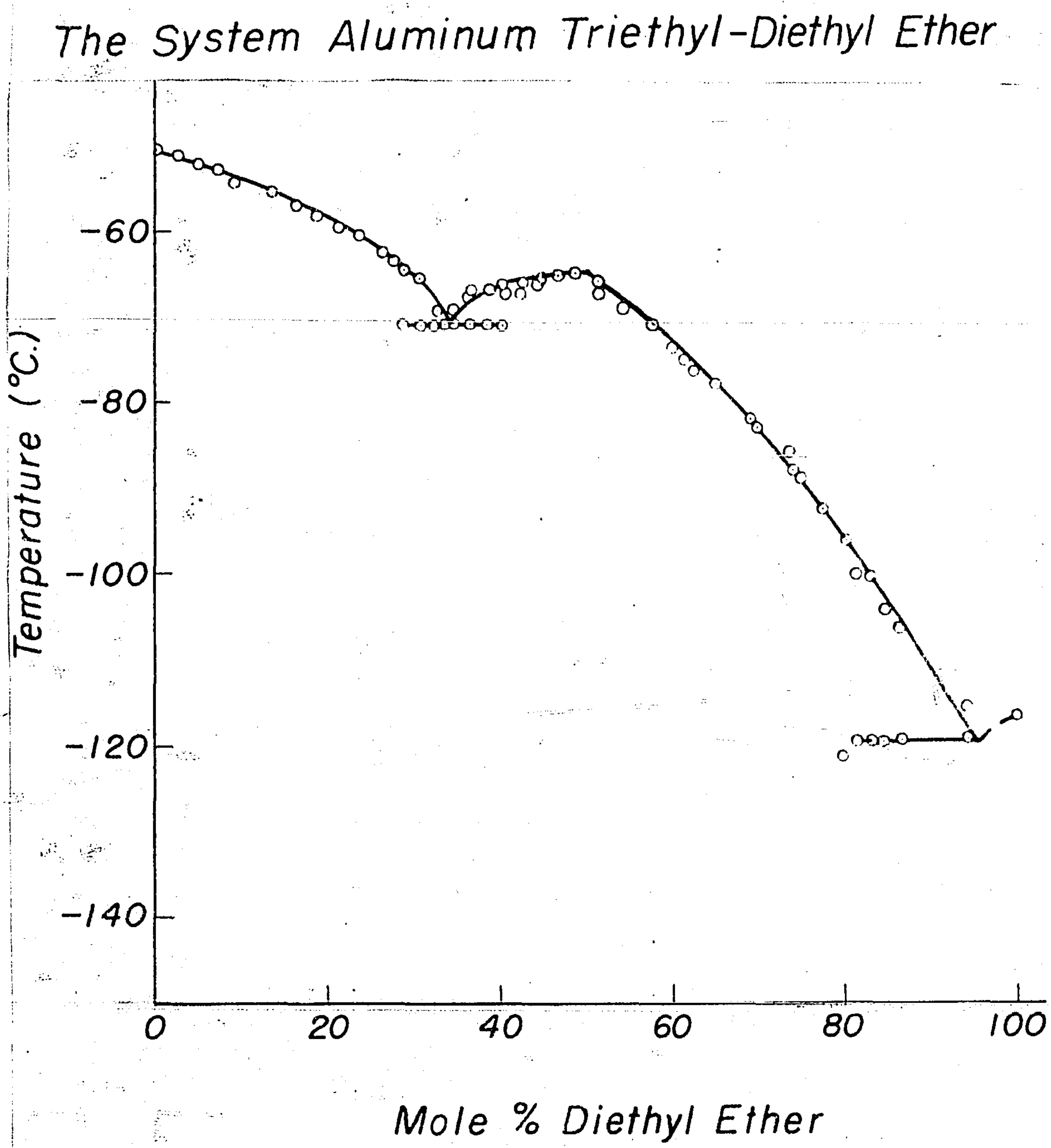

The System Aluminum Triethyl-Diethyl Ether
Temperature (°C.)
-60
-80
-100
-120
-140
0
20
40
60
80
100
Mole % Diethyl Ether

FIGURE 4

TABLE I

THE SYSTEM ALUMINUM TRIETHYL—DIETHYL ETHER

Mole Percent $(C_2H_5)_2O$	Freezing Point (°C)	Eutectic Temperature (°C)
0.00	-50.3 -50.7	
2.51	-51.6	
5.18	-52.1	
7.53	-52.8	
9.23	-54.4	
13.67	-55.2	
16.16	-57.0	
18.76	-58.1	
21.09	-59.8	
23.60	-60.5	
26.40	-62.5	
28.00	-64.0	
28.84	-64.8	-71.0
30.36	-65.5	
30.83	-65.5	-70.9
32.40	-69.3	-71.0
32.58	-69.5	-71.0
33.75		-71.0
34.50	-69.0	-70.8
36.34	-67.5	-70.9
36.79	-67.0	-70.5
38.20	-66.5	-71.0

Table I (cont...)

Mole Percent $(C_2H_5)_2O$	Freezing Point (°C.)	Eutectic Temperature (°C.)
40.22	-67.0	-70.8
40.30	-66.0	
42.29	-67.0	
42.86	-66.2	
44.53	-66.2	
45.12	-65.3	
46.77	-65.2	
48.94	-65.0	
51.08	-66.1	
51.33	-66.8	
54.10	-69.0	
57.40	-70.8	
59.87	-73.8	
61.06	-75.1	
62.69	-76.5	
65.05	-77.5	
69.01	-82.0	
69.18	-82.4	
69.85	-82.3	
73.38	-85.7	
73.99	-87.6	
74.84	-88.5	
77.33	-92.1	
80.01	-96.0	-120.9

Mole Percent $(C_2H_5)_2O$	Freezing Point (°C.)	Eutectic Temperature (°C.)
81.16	-100.1	-119.2
82.95	-100.6	-119.6
84.52	-104.2	-119.1
86.16	-106.3	-119.2
94.09	-115.2	-119.2
100.00	α -116.0 β -123.5	

50 mole per cent of diethyl ether. The compound has the empirical composition $Al(C_2H_5)_3 \cdot (C_2H_5)_2O$. The diagram indicates that the compound is considerably dissociated at its freezing point since the maximum is not sharp. There are eutectics at 34 mole per cent of ether, -71.0°C., and at 96 mole per cent of ether, -119.1°C.

The data obtained on the etherate are shown in Table II. The freezing point of the pure etherate is -64.0°C., -64.5°C. The freezing points obtained after ether additions had been made fit the curve very closely if it is assumed that the etherate is the 1:1 compound.

Conclusions. The maximum in the freezing point curve of the system aluminum triethyl-diethyl ether occurs at 50 mole per cent of each component. However, because of the experimental difficulties in taking points in this system and the nearness of the eutectic temperature (-71°C.) to the freezing point (-65°C.) of the compound there is still room for some small doubt concerning the 4:3 and 1:1 alternatives. However, the facts that samples of the etherate, purified as carefully as possible, gave freezing points agreeing well with the maximum in the freezing-point curve, and that the changes in freezing point of these samples produced by the additions of known quantities of ether fit the curve closely if it is assumed that the etherate is a 1:1 compound remove any doubt concerning this point. Finally, aluminum analyses on the pure etherate (see Table II) agree closely with the calculated value for the 1:1 compound.

TABLE II

	MOLE PERCENT ETHER		FREEZING POINT (°C.)	PERCENT ALUMINUM (By analysis)	PERCENT ALUMINUM (Calculated)	
	Assuming a 1:1 compound	Assuming a 4:3 compound			1:1 compound	4:3 compound
Etherate (Preparation I)	50.00	42.86	-64.0	14.31	14.33	15.89
Preparation I after first ether addition	56.28	50.22	-67.5			
Preparation I after second ether addition	65.14	60.53	-75.5			
Etherate (Preparation II)	50.00	42.86	-64.5	14.46	14.33	15.89
Preparation II after first ether addition	56.25	50.19	-68.6			
Preparation II after second ether addition	66.16	61.70	-77.5			

D. Reaction of Aluminum Triethyl Etherate with Alkali Metal Alkyls

Grosse and Mavity[29] reported at the 96th meeting of the American Chemical Society that they had prepared lithium, sodium, and potassium aluminum tetraethyls by the reaction of the alkali metal alkyl with aluminum triethyl and by the reaction of the alkali metal with aluminum triethyl. No experimental details were given in the abstracts of the meeting nor has the work ever been published. Earlier workers had prepared these compounds in aluminum triethyl solutions, but, though they realised they had what they called "solvates" or "autocomplexes" they did not isolate them[20]!

Hurd has reported the preparation of lithium aluminum tetramethyl from lithium methyl and aluminum trimethyl etherate[24]. Wittig and Bub have reported the preparation of $Li(AlPh_4)$ which crystallizes with two or three moles of diethyl ether, or with one mole of tetrahydrofuran, or with five moles of dioxane. They also reported the preparation of $Na[AlPh_3(CPh_3)]$ [30].

No synthesis has ever been published for lithium aluminum tetraethyl or sodium aluminum tetraethyl.

In this research sodium aluminum tetraethyl was prepared from sodium ethyl and aluminum triethyl etherate, and lithium aluminum tetraethyl from lithium ethyl and aluminum triethyl etherate.

Preparation of Sodium Ethyl. The procedure used was a modification of those of Whitmore and Zook[31] and Gilman and Young[32]. The apparatus consisted of a 500-ml., 3-neck flask equipped with a condenser, pressure-equalizing dropping funnel, nitrogen inlet and outlet, and magnetic stirrer. One hundred and fifty ml. of petroleum ether, (65-100°C. boiling range) free of unsaturates, was added and the flask swept with nitrogen. Ten grams of sodium metal was added in large pieces and the flask cooled to below 20°C. with an ice bath and kept there during the dropwise addition of 20 g. of mercury diethyl. The funnel was rinsed with 50 ml. of petroleum ether, the flask allowed to warm to room temperature and stirring continued for two days.

Preparation of Sodium Aluminum Tetraethyl. The aluminum triethyl etherate used in the preparation was made as described earlier. However, it is important that this product be free from excess ether in order to reduce the possibility of subsequent significant loss of sodium ethyl by cleavage of the ether. Therefore, the aluminum triethyl etherate was heated in an oil bath at 60°C., under nitrogen atmosphere, for one hour to distill off any traces of ether.

The flask containing the sodium ethyl was then cooled with an ice bath and 41 ml. (a slight excess) of aluminum triethyl etherate added dropwise with stirring. The funnel was rinsed with 50 ml. of petroleum ether (65-100°C. boiling range) and stirring continued for three hours. The solution was then filtered into a 500-ml. 3 neck flask through a filter stick (Ace Glass Co. porosity D) and the residue washed three times with 50-ml. portions of petroleum ether. The solvents were then distilled off, using an oil bath to heat the flask. The bath temperature was kept at 110°C. for ten minutes after the distillation stopped. The contents were then heated under vacuum for one-half hour with the bath at 110°C. This additional heating seems to be necessary to remove the ether from the sodium aluminum tetraethyl. The mixture was then cooled, 150 ml. of benzene added, and refluxed for one hour. It was then filtered while hot through a filter stick (Ace Glass Co. porosity C) into a 250-ml. 1-neck flask, and rinsed through with 25 ml. of benzene. The benzene was then distilled off until approximately 100 ml. of solution remained. On standing crystals separated from this solution. Crystallization sometimes is slow, several days being required. The mixture was then cooled to 10°C. and filtered. The crystals were washed twice with 15-ml. portions of benzene and twice with 15-ml. portions of petroleum ether (30-60°C. boiling range) and dried under vacuum. If the crystals were yellow they were recrystallized again from benzene. The yield, after two recrystallizations, was about 10 grams.

Analysis. The product was weighed directly in the flask in which it had been recrystallized. It was dissolved in diethyl ether, the ether solution cooled in an ice bath and hydrolyzed by small additions of water. The mixture was then acidified with hydrochloric acid and warmed to evaporate the ether and to speed solution of the aluminum hydroxide and oxide. The solution was diluted to a suitable volume and aliquot parts were taken. Aluminum was precipitated and weighed as the 8-hydroxyquinolate[28]. Sodium in the filtrate was converted to the sulfate and weighed as such. In the determination of sodium, ammonium carbonate was added to the residue between ignitions to convert any acid sulfate to sulfate.

	Aluminum		Sodium	
	Found	Calculated for $NaAl(C_2H_5)_4$	Found	Calculated for $NaAl(C_2H_5)_4$
1st Preparation	16.11%	16.23%	13.89%	13.84%
2nd Preparation	16.18		14.02	

Properties. Sodium aluminum tetraethyl is a white crystalline solid which reacts violently with water, decomposing to oxide and hydroxide with gas evolution. The compound is highly soluble in diethyl ether, much less soluble in benzene, and still less soluble in petroleum ether. It was found to melt, without sublimation, in an evacuated flask at about 125°C.

Preparation of Lithium Ethyl. Lithium ethyl was prepared by a modification of the procedure of Perrine and Rapoport[33], the principal change being that a simplified apparatus with a mercury-seal stirrer and continuous flow of helium was used. Two hundred fifty ml. of mineral oil was purified by vigorously stirring it with molten lithium under a helium atmosphere using a Hershberg stirrer. The mineral oil was then filtered into a 1-liter, 3-neck flask through a plug of glass wool in the end of a constricted glass tube, using a slight suction and maintaining the helium flow so that air was not drawn in through the stirrer. When an aspirator was used to furnish suction a Drierite tower was necessary to guard against back-diffusion of water vapor. Lithium sand was then prepared in this mineral oil from 4.5 g. of lithium. A 1-liter 3-neck flask was used for this reaction; it was equipped with a helium outlet, a mercury-seal stirrer, and a pressure-equalizing dropping funnel which contained 275 ml. of petroleum ether (30-60°C. fraction, unsaturates-free) and whose stopper contained the helium inlet. The oil was filtered off as before and the lithium sand was washed with three 75-ml. portions of petroleum ether. Fifty ml. of the petroleum ether was then added to the sand and one or two ml. of ethyl bromide (ether-free) was added with rapid stirring to initiate the reaction. The remainder of the 15 ml. of ethyl bromide, dissolved in 300 ml. of petroleum ether, was added dropwise over a period of one and one-half hours. The dropping funnel was rinsed with 50 ml. of petroleum ether and the mixture was stirred for one hour.

Preparation of Lithium Aluminum Tetraethyl. Forty-one ml. of aluminum triethyl etherate was added dropwise with stirring to the flask containing the lithium ethyl, and 50 ml. of petroleum ether was used to rinse the dropping funnel. Three hundred ml. of benzene was then added and all of the petroleum ether distilled off. An additional 200 ml. of benzene was added and the mixture was refluxed for 15 minutes. The solution was filtered while hot through a filter stick (Ace Glass Co. porosity C) into a 1-liter, 1-neck flask. Then 200 ml. of benzene was distilled off and the hot solution was filtered through a filter stick (Ace Glass Co. porosity D) into a 500-ml. flask, previously weighed with stopper.

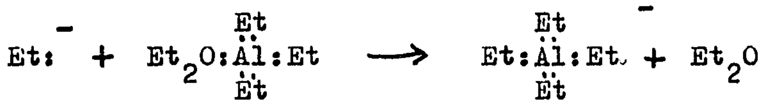
Benzene was distilled off until about 75 ml. of solution remained. The solution was cooled to about 10°C. and the benzene was filtered off the crystals through a filter tube. The crystals were washed three times with 50-ml. portions of cold (ice-salt bath) petroleum ether (30-60°C. boiling range) and dried under vacuum. The yield in a typical experiment was approximately nine grams.

Analysis. This compound was prepared for analysis in the same way as was the sodium aluminum tetraethyl. Aluminum was determined gravimetrically as the 8-hydroxyquinolate[28] and lithium as the sulfate on the filtrate.

	Aluminum		Lithium	
	Found	Calculated for $LiAl(C_2H_5)_4$	Found	Calculated for $LiAl(C_2H_5)_4$
1st Preparation	17.42%		4.48%	
2nd Preparation	17.42	17.96%	4.66	4.62%
3rd Preparation	17.86		4.69	

Properties. Lithium aluminum tetraethyl is a white solid, forming needle-like crystals, radiating from a central point and appearing under the microscope as smooth, round rods. It is similar in properties and solubility to the sodium compound except that it melts with sublimation in an evacuated flask at about 160°C.

Conclusions. The compounds sodium ethyl and lithium ethyl contain the strong Lewis base, the ethide ion, which, in these reactions, replaces the ether molecule which had been coordinated, through its oxygen atom, to the aluminum atom of aluminum triethyl:



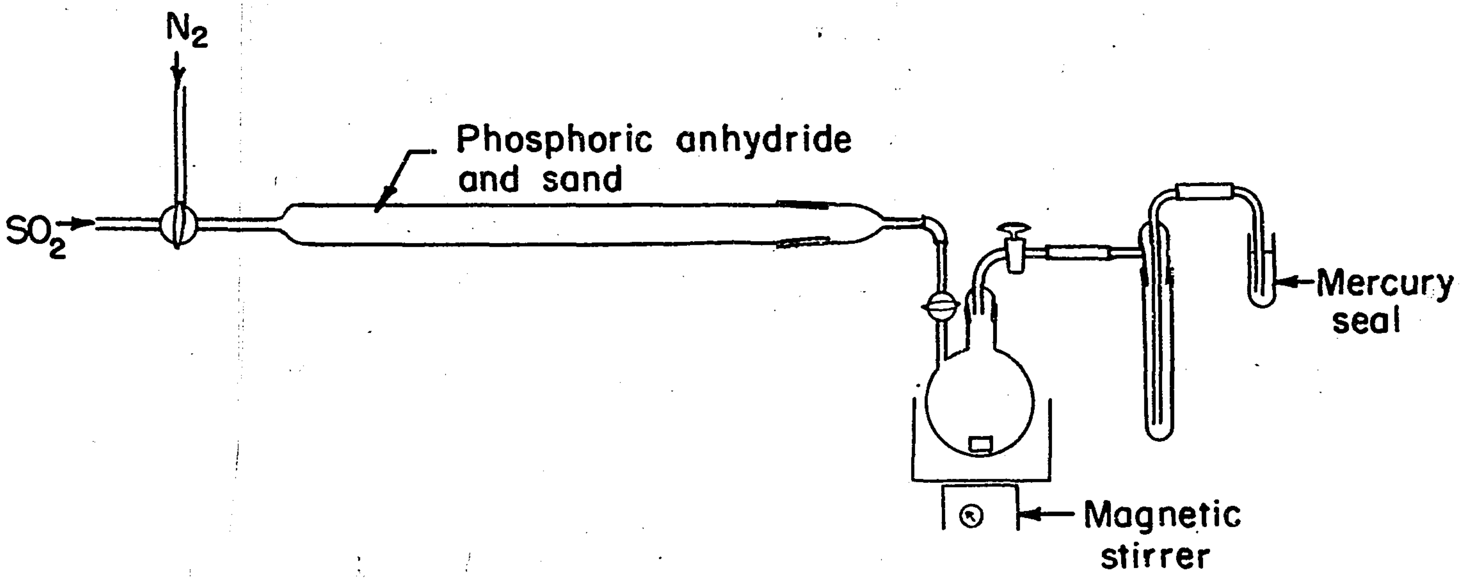
$$\overset{-}{\text{Et}:} + \text{Et}_2\text{O}:\overset{\text{Et}}{\underset{\text{Et}}{\ddot{\text{Al}}}}:\text{Et} \longrightarrow \text{Et}:\overset{\text{Et}}{\underset{\text{Et}}{\ddot{\text{Al}}}}:\text{Et}^{-} + \text{Et}_2\text{O}$$

Thus, the salts $Na[Al(C_2H_5)_4]$ and $Li[Al(C_2H_5)_4]$ have been prepared, isolated, and analyzed.

E. Reaction of Aluminum Triethyl Etherate with Sulfur Dioxide.

Procedure. The reaction of aluminum triethyl etherate with sulfur dioxide was carried out three times in order to obtain sufficient pure material for identification, tests, and preparation of derivatives. All three runs were quite successful and although there were slight variations in procedure, the following is typical:

A 100-ml. round bottom flask with a ground-glass joint and with a side arm bearing a stopcock was used as the reaction flask (Fig. 5). The joint that was fitted into the top of the flask also had a stopcock and the outlet was protected by drying tubes or a mercury seal. The apparatus was swept out with nitrogen and 10 ml. of aluminum triethyl etherate (measured by pipet) was placed in the reaction flask while the nitrogen flow was continued. Sulfur dioxide was dried by condensing it, by use of a Dry-Ice-acetone bath, into a trap containing phosphoric anhydride, or by passing the vapor through a tube containing a mixture of phosphoric anhydride and sand. The reaction flask containing the aluminum triethyl etherate was surrounded by a Dry Ice-acetone bath. The nitrogen flow was stopped, the exit stopcock closed and the inlet was connected to the trap containing the liquid sulfur dioxide which had been shaken with the phosphoric



APPARATUS FOR SULFUR DIOXIDE REACTION

FIGURE 5

anhydride. The trap was allowed to warm. Sulfur dioxide condensed on the aluminum triethyl etherate and when the flask was shaken a vigorous reaction took place. In one run a magnetic stirrer was used, and this gave much better stirring. A greenish-yellow crystalline solid was formed. The excess sulfur dioxide was vaporized by allowing the flask to warm to room temperature. No liquid remained. Dry nitrogen was run over the product by passing it into the flask until no noticeable sulfur dioxide odor was given off. The crystals appeared only faintly yellow then, and were dry and granular. The product was dried overnight under vacuum and was then completely white. No further purification was done.

The product from this reaction was identified by analysis and derivatives as aluminum ethyl sulfinate.

Analysis. The analysis is complicated by the fact that the salt is rapidly hygroscopic and that the sulfur content is not easily oxidized completely to sulfate, bromine being ineffectual for this purpose. Oxidation was accomplished, however, with a Parr peroxide bomb or by the Carius method.

	Found	Calculated for $Al(SO_2C_2H_5)_3$
Aluminum (as Al_2O_3 residue on ignition)	8.72% 8.80 9.02	8.80%
Aluminum (as 8-hydroxyquinolate)	8.70	8.80
Sulfur	31.51 31.12	31.40
Carbon	23.38 23.42	23.52
Hydrogen	4.99 4.94	4.94

The disulfone derivative (1,2 diethylsulfonyl ethane, $C_2H_5SO_2C_2H_4SO_2C_2H_5$) was prepared by a modification of Allen's procedure[34]. Attempts to use the aluminum salt in n-butyl alcohol or n-propyl alcohol were unsuccessful. However, after conversion to the sodium salt (using either saturated aqueous or alcoholic sodium hydroxide) a successful preparation was obtained, using ethyl alcohol as solvent. The following procedure was used:

One and four-tenths grams of aluminum ethyl sulfinate was converted to the sodium salt by treatment with alcoholic sodium hydroxide and the resulting aluminum hydroxide removed by filtration, followed by washing with ethyl alcohol until the volume of the filtrate was 15-20 ml. Two ml. of ethylene bromide was added and the solution refluxed for ten hours. It was then poured into water and the disulfone filtered off and recrystallized from ethyl alcohol. The derivative consisted of white, glistening, needle-like crystals. The yield after recrystallization was 40-45%.

The melting point was 136°C. as compared with value given in the literature, 136-137°C.[34]

The diethyl sulfone derivative ($C_2H_5SO_2C_2H_5$) was made using Allen's procedure, modified slightly[34]. Approximately one gram of aluminum ethyl sulfinate was converted to the sodium salt by treatment with an ethyl alcohol-water solution of sodium hydroxide. The resulting aluminum hydroxide was filtered off, and the precipitate was washed with enough alcohol to bring the volume up to about 75 ml. Two ml. of ethyl iodide was added to the solution and it was refluxed overnight. No precipitate of diethyl sulfone formed when water was added to this solution, so the solution was extracted with carbon tetrachloride. The carbon tetrachloride solution was filtered and evaporated, leaving white crystals of diethyl sulfone. These were recrystallized from ethyl alcohol. The melting point was found to be 71-72°C.; the melting point given in the literature is 71°C.[35]

Conclusions and Discussion. The product of the reaction of sulfur dioxide with aluminum triethyl etherate is aluminum ethyl sulfinate. The reaction can be represented:

$$SO_2 + (C_2H_5)_2O:Al(C_2H_5)_3 \longrightarrow (C_2H_5SO_2)_3Al + (C_2H_5)_2O$$

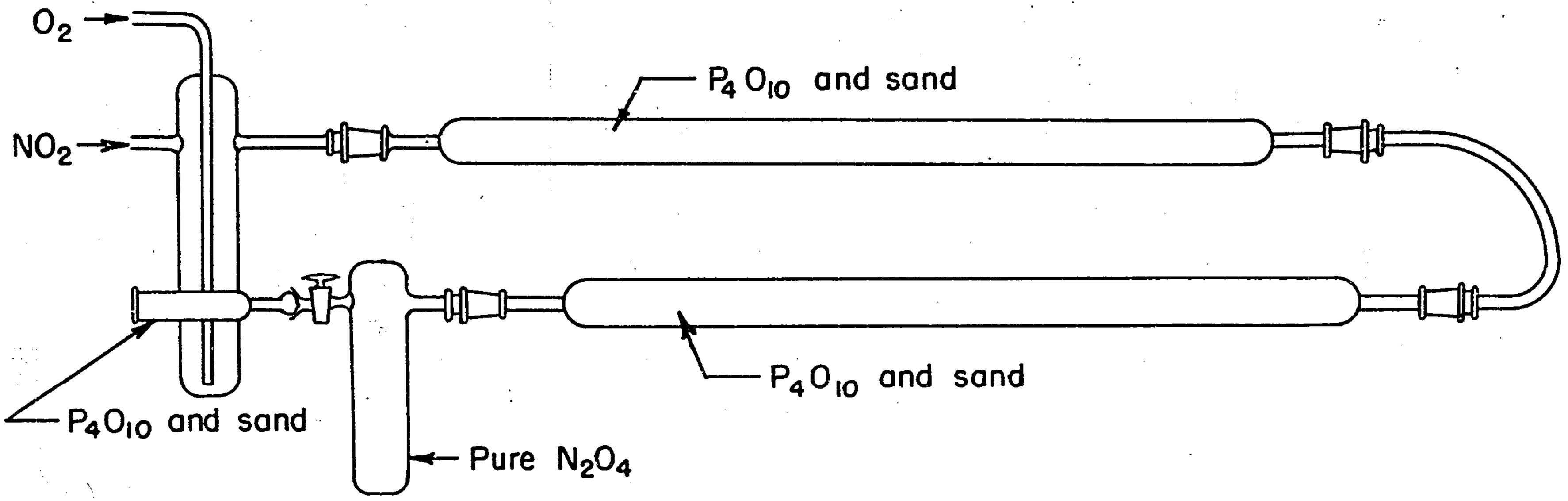
This reaction was found to be analogous to that of Grignard reagents[36] and zinc alkyls[37] with sulfur dioxide. However, the yield is in this case nearly quantitative, while much lower (50-60%) yields are often obtained with Grignard reagents[36].

F. Reaction of Aluminum Triethyl Etherate with Nitrogen Dioxide.

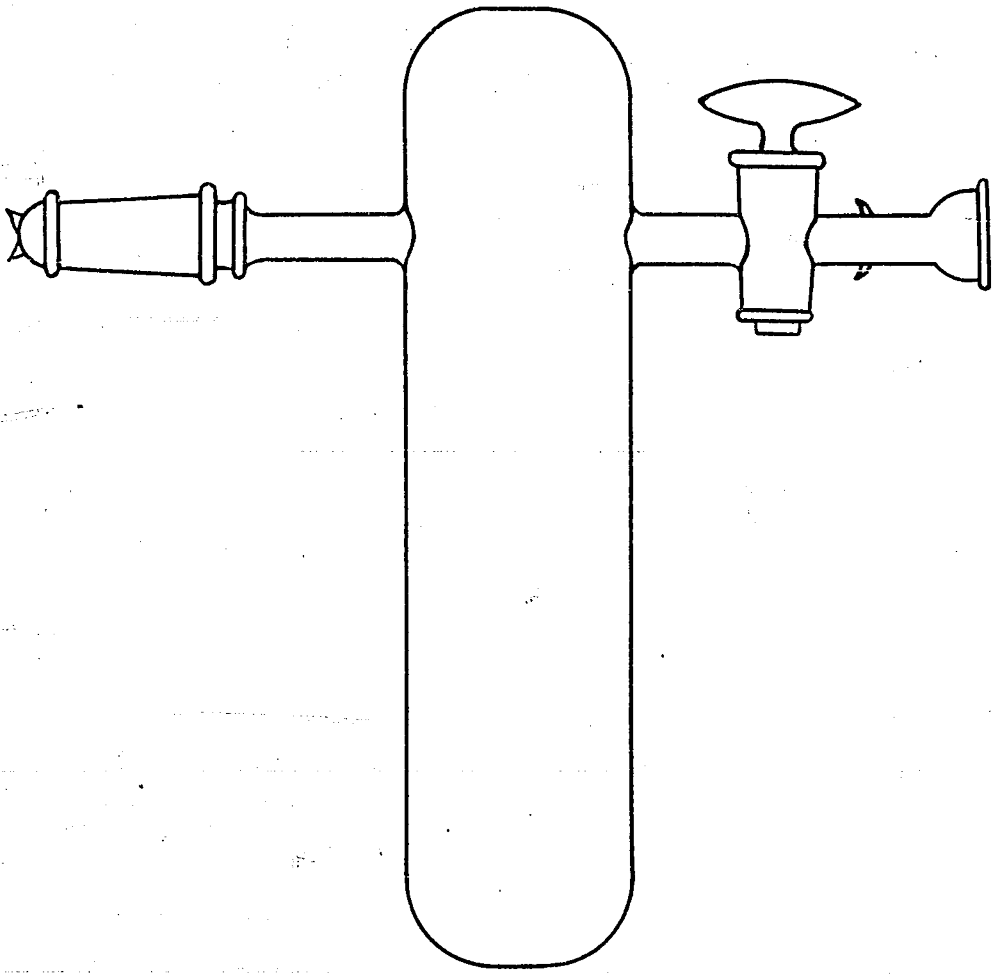
Procedure. The product of the reaction with nitrogen dioxide was difficult to identify and it was necessary that the reaction be run four times before enough was found out about the product so that it could be efficiently separated and positively identified.

The reaction was carried out in a 500 ml. flask with a ground-glass joint at the top and a small side arm with a ball joint near the top. A bridge, consisting of a three-way stopcock with ball joints on two arms was attached by one of the ball joints to the side arm. The other ball joint fitted one arm of a transfer cell which was used to collect and store liquid dinitrogen tetroxide. A ground-glass joint with a stopcock was placed in the ground-glass joint at the top of the flask. The reaction flask contained a glass-enclosed iron slug, so that when a motor-rotated magnet was placed below, stirring was effected. All joints were held together with clamps or rubber bands.

Dinitrogen tetroxide (Matheson Co.) was purified by a method similar to that of Giauque and Kemp[38] in an all-glass apparatus (Fig. 6). The commercial dinitrogen tetroxide was frozen by use of a bath of Dry Ice-acetone. It was melted, then freed of lower oxides of nitrogen by bubbling oxygen through the liquid while the container was surrounded by an ice bath. This was continued until the dark-green liquid became orange-red. The bath was then removed, the oxygen flow continued, and the nitrogen dioxide was distilled, through drying tubes containing a mixture of phosphoric anhydride and sand, into the transfer cell mentioned above (Fig. 7), where it



DINITROGEN TETROXIDE PURIFICATION APPARATUS
FIGURE 6



DINITROGEN TETROXIDE TRANSFER CELL

FIGURE 7

was frozen, using a Dry Ice-acetone bath. The liquid dinitrogen tetroxide was stored under its own vapor pressure in the transfer cell in a refrigerator. Graphite from a soft pencil, together with a small amount of Silicone vacuum grease, was used as a lubricant on all joints and stopcocks contacted by the nitrogen dioxide.

The following procedure was followed in making a run. The reaction flask was swept out with nitrogen, which entered from one of the arms of the bridge through the side arm of the reaction flask and left at the top of the flask. With the nitrogen still flowing, the joint at the top of the flask was removed and 25 ml. of aluminum triethyl etherate was added, followed by approximately 250 ml. of diethyl ether. The joint at the top of the flask was replaced, the stopcock on it was closed, and the nitrogen flow was stopped. The dinitrogen tetroxide container was weighed and then connected to the bridge. The reaction flask was cooled in a Dry Ice-acetone bath, stirring was begun, and the bridge stopcock was opened, allowing nitrogen dioxide to enter the reaction flask. At times white solid collected on the cool sides of the flask. When this solid was warmed with the fingers, white fumes appeared. Occasionally, bluish-green solid appeared on the sides and once the entire solution became bluish-green, but this color quickly disappeared. When approximately the desired quantity of nitrogen dioxide had distilled as judged by the lowering of the liquid level in the transfer cell, the bridge stopcock was closed and the transfer cell removed and weighed. Approximately 5 g. of nitrogen dioxide was used in a run. The solution was yellow-brown at the end of the run. The stopcock on the joint at the top of the flask was opened through a drying tube and the reaction mixture was allowed to warm to room temperature and then stood for several hours. The flask was then cooled in an ice bath and the excess aluminum triethyl etherate was hydrolyzed, using a minimum of water. The paste or slurry which resulted was extracted with ether in a continuous extractor. Potassium hydroxide was added to the slurry after it had been extracted for some hours and the extraction was continued. The ether extracts were dried several days over barium oxide, the barium oxide was filtered off, and the ether was distilled off. Four and six-tenths grams of liquid remained. The reaction product was vacuum distilled, the receiver being cooled with Dry Ice-acetone.

The liquid product was colorless or light yellow when freshly distilled, but seemed to darken gradually on standing or warming. It was basic to litmus, and reduced ammoniacal silver nitrate. The boiling point, taken using a semi-micro distilling flask, was 132-134°C., but some decomposition took place as there was a black residue remaining. The refractive index taken using a Beckman model of an Abbe refractometer was 1.416 at 26.5°C. One neutral equivalent determination, using a pH meter to determine the equivalence point, gave a value of 97. The oxalate derivative was made by using anhydrous oxalic acid and it was recrystallized from methyl alcohol.

It had a melting point of 135-138°C. Several attempts were made to obtain the hydrochloride and the hydrobromide but these were unsuccessful, as the derivatives did not crystallize in a reasonable time, but remained as oils, darkening gradually. The infrared spectrum was run on a Baird Associates' Recording Infrared Spectrophotometer, using a rock salt sandwich cell. The liquid was used without a solvent. The peaks are listed in Table III.

In order to compare the infrared spectrum of the reaction product with that of N,N-diethylhydroxylamine, $(C_2H_5)_2NOH$, which was what the product was thought to be, some N,N-diethylhydroxylamine was prepared from diethylamine and hydrogen peroxide using the method of Dunstan and Goulding[39]. Sixty-six grams of diethylamine was cooled in an ice bath. Ninety-five grams of 30% hydrogen peroxide solution was added dropwise with stirring. There was no evidence of reaction. After all the hydrogen peroxide was added, the bath was removed and the flask was allowed to warm to room temperature. After about thirty to sixty minutes, the reaction became vigorous but then quieted. It was allowed to stand with stirring for twenty-four hours. The solution was made basic with sodium hydroxide and extracted with ether. The ether extracts were dried over barium oxide, the barium oxide filtered off, and the ether distilled. The liquid residue remaining was vacuum distilled. The boiling point of the distillate, taken by the micro method, was 134°C. The refractive index, taken on a Beckman model of an Abbe refractometer, was 1.424 at 27°C. The product was basic

TABLE III

INFRA-RED SPECTRA

N,N-Diethyl Hydroxylamine (Prepared)	Reaction Product
Wave-length (microns)	Wave-length (microns)
3.08	3.10
3.38	3.42
3.50	3.48
3.55	3.58
5.97	
6.08	
6.88	6.90
7.22	7.25
7.40	7.42
	7.64
	7.88
8.48	8.45
8.78	8.78
9.25	9.26
9.48	9.48
9.62	9.63
10.94	10.95
13.14	13.14

to litmus and reduced ammoniacal silver nitrate. The infrared spectrum data are given in Table III.

Results. The results on the identification of the product are summarized in Table IV.

Discussion. The summary of properties in Table IV leaves no doubt that the reaction product is N,N-diethylhydroxylamine. Some of the analytical values are poor because it was not realized that the material had partly decomposed from standing. The two infrared spectra are essentially the same, but each sample contained an impurity not present in the other.

In this reaction aluminum triethyl etherate behaves similarly to a Grignard reagent since ethyl magnesium iodide when reacted with nitrogen dioxide also yields N,N-diethylhydroxylamine[40].

G. Reaction of Aluminum Triethyl Etherate with Nitric Oxide.

Procedure. Nitric oxide was made by Winkler's method[41], improved by Moser[42] and by Johnston and Giauque[43]. The gas was generated by dropping 50% sulfuric acid (1:1) into a solution that was 4 molar in potassium nitrite and 1 molar in potassium iodide. The solution in the gas generator was kept stirred by use of a glass-enclosed iron slug which was rotated by attraction of a motor-rotated magnet underneath. The gas generator and pressure-equalizing dropping funnel were so constructed as to minimize "dead" space. The generator also had an inlet with a stopcock so the generator and purification train could be swept with nitrogen. The reaction for the formation of nitric oxide is:

TABLE IV

	N,N-Diethyl Hydroxylamine (Prepared)	Reaction Product	N,N-Diethyl Hydroxylamine (Literature)
Physical Properties:			
State and color	Slightly yellow liquid	Clear, colorless liquid	Clear liquid
Boiling point	134°C.	132-134°C.	130-134°C.
Melting point		-8 to -15°C.	about -10°C.
Refractive index	1.424	1.416	
Solubility	Soluble in water to give a solution alkaline to litmus. Soluble in ether.	Soluble in water to give pH 8. Soluble in ether.	Soluble in water to give a slightly alkaline solution. Soluble in ether.
Chemical Properties:			
Ammoniacal silver nitrate	Reduces	Reduces	Reduces
Neutral equivalent		97 (one determination)	89.1
Analysis:			
Carbon (%)		53.72, 53.93	53.89
Hydrogen (%)		11.82, 11.89	12.44
Nitrogen (%)		14.70, 14.93	15.72
Derivatives:			
Oxalate		135-138°C.	137-139°C.
Hydrochloride		Oily, could not be crystallized.	Difficult to crystallize.
Hydrobromide		Could not be crystallized.	Difficult to crystallize.
Chloroplatinate		Reduced to Pt.	Reduced to Pt.
Infrared spectrum:		Reaction product agrees with that of prepared diethylhydroxylamine.	

$$2HNO_2 + 2I^- + 2H^+ \longrightarrow 2NO + I_2 + H_2O$$

The nitric oxide was passed through a purification train which consisted of:

1) a fritted-disc gas-washing bottle filled with 90% sulfuric acid to remove excess water,

2) a gas-washing bottle, with glass beads to break up the bubbles, filled with 50% potassium hydroxide, to remove nitrogen dioxide, and iodine,

3) a trap cooled to -75°C. to remove iodine, nitrogen dioxide, water,

4) a tower containing a mixture of phosphoric anhydride and sand to remove water.

All stoppers were secured and liberally coated with Glyptal, since it took considerable pressure to force the nitric oxide through the train. This procedure should yield a gas that is 99.6% pure, with nitrous oxide as the principal impurity. Two hundred grams of potassium nitrite and 100 g. of potassium iodide, dissolved in 600 g. of water, made up the solution in the generator. Three hundred fifty ml. of 1:1 sulfuric acid was added from the dropping funnel. These amount of reagents give 0.6 moles of nitric oxide, which was the amount used in a run.

A 500-ml. three-neck flask was used for the reaction. Through one neck an inlet tube, which ended below the surface, entered. An efficient condenser was placed in another neck of the flask, with a stopcock at the condenser exit. The gases passed out of the system through a mercury seal. Stirring was effected by use of a glass-enclosed iron slug driven by a motor-rotated permanent magnet placed underneath the flask.

The apparatus and train were swept out thoroughly with nitrogen. Any oxygen that remained would give rise to difficulties, since nitric oxide reacts with oxygen to give nitrogen dioxide, which in turn reacts quickly with aluminum triethyl etherate. The stop-cock at the end of the condenser was closed in order to give a good current of nitrogen through the third neck of the flask and 10 ml. of aluminum triethyl etherate was added, followed by 200 ml. of ether. The stopper was replaced, the stopcock on the condenser opened, and the addition of sulfuric acid to the solution in the generator was begun. The reaction was carried out at room temperature. It was found that the nitric oxide reacted very slowly and, in the most successful run, nitric oxide was bubbled through for seven and one-half hours, and the reaction mixture was allowed to absorb the gas overnight. The apparatus and reaction flask were swept free of remaining nitric oxide with nitrogen. The reaction mixture was diluted with ether, cooled with an ice bath, and hydrolyzed with ice water. It was then made acid with 1:1 sulfuric acid and extracted with ether. The ether extracts were treated with a slurry of freshly precipitated and thoroughly washed hydrous copper oxide. The reaction mixture was also extracted with benzene and the benzene extracts treated with copper oxide. The excess copper oxide was filtered off, and the filtrates evaporated at room temperature at reduced pressure.

Purple, needle-like crystals remained. These purple crystals were extremely soluble in benzene, less soluble in ether, and even less soluble in water. They decomposed on warming. They were mixed with some white material which was highly water soluble, but not so soluble in benzene. The crystals were then dissolved in a little benzene and filtered from the white material. The benzene was evaporated and the crystals were dried under vacuum. The yield seemed to be dependent on the time that the reaction mixture was in contact with nitric oxide and was 4.6 g. in the most successful run.

In one run a small amount of the ether extracts was tested for a nitroso grouping, using the Liebermann nitroso test. The colors of a positive test appeared but they lasted only a few seconds.

The product was thought to be ethylnitrosohydroxylamine, $C_2H_5N(NO)OH$. The absorption spectrum (visible) was run on a water solution of the copper salt using a Beckman DU Spectrophotometer with Corex cells. However, the spectrum the compound gave was not suitable for its identification. Neither is the very poor spectrum of Franchimont and Backer[43a] on copper ethylnitrosohydroxylamine suitable for identification. The spectrum taken in this work agrees with their spectrum as well as can be determined, but the agreement proves little.

The copper salt was crystallized from benzene and then from water, discarding the mother liquor each time. The crystals were dried under reduced pressure for about one hour. The compound was analyzed and gave the following results: carbon, 20.09%, 19.99%; hydrogen, 4.16%, 4.21%; nitrogen, 23.18%, 23.00%; copper (by residue on ignition, low because of loss of ash), 25.42%, 25.82%. Calculated for copper ethylnitrosohydroxylamine (anhydrous): carbon, 19.87%; hydrogen, 4.17%; nitrogen, 23.18%; copper, 26.30%. This salt is reported in the literature as having one-half mole of water of crystallization when obtained from water solution[44].

Discussion. Very little work has been done with nitrosohydroxylamines and, particularly, with ethylnitrosohydroxylamine, $C_2H_5N(NO)OH$. The lack of information on the properties of this compound and its salts made positive identification difficult.

The reaction of aluminum triethyl etherate with nitric oxide is analogous to that of zinc diethyl with nitric oxide as a salt of ethylnitrosohydroxylamine is formed in this case, also[44]. It is interesting to note that, though the reaction takes place at room temperature, dimerization of the nitric oxide is indicated to account for the nitrogen-nitrogen bonding in the product. Karrer and Schwyzer[45] assumed dimerization of the nitric oxide to account for the formation of hyponitrous acid by the reaction of lithium aluminum hydride and nitric oxide, followed by hydrolysis.

H. The Reaction of Aluminum Triethyl Etherate with Pyridine.

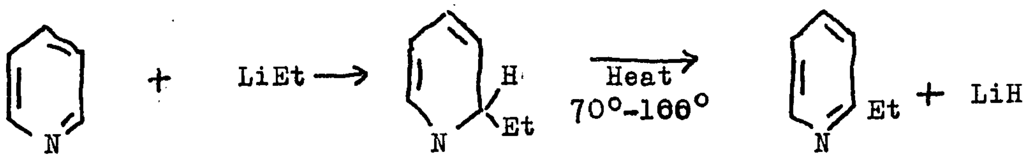
Procedure. Approximately 5 ml. of aluminum triethyl etherate was distilled under vacuum into a 100-ml. flask containing a glass-enclosed magnetic stirring bar. Pyridine (Baker's C.P. Analyzed) which had been standing for several days over barium oxide, was distilled from barium oxide under nitrogen atmosphere into a pressure-equalizing dropping funnel. A glass connector, with a side arm for nitrogen inlet, was placed between the flask and the dropping funnel. The nitrogen outlet was at the top of the dropping funnel. The flask containing the etherate was cooled with Dry Ice-acetone, and approximately 50 ml. of pyridine was added slowly, with stirring. The reaction mixture was allowed to warm to room temperature, and the flask was stoppered with a ground-glass joint with a vacuum stopcock. The excess pyridine was evaporated under a vacuum, with stirring, and protection from light. This evaporation was continued until the flask was losing weight at an approximately constant slow rate and until small amounts of aluminum were detected in the trap. The product was weighed in the flask. The freezing point was found to be about -41°C.; it was determined using a copper-constantan thermocouple on a Leeds and Northrup Micromax. Excessive supercooling decreased the accuracy of this freezing point determination. The product was an amber colored liquid which decomposed, becoming bright red and precipitating a solid, before boiling at ordinary pressures.

For analysis the product was diluted with ether and hydrolyzed under reflux to minimize loss of pyridine. The solution was acidified with hydrochloric acid and heated to free it of ether. It was diluted to a suitable volume and aliquot parts were taken for the aluminum analysis and for the pyridine analysis.

Aluminum was precipitated and weighed as the 8-hydroxyquinolate after it had been determined, by running a known sample with pyridine added, that pyridine did not interfere with this method. Found: 14.24% Al. Calculated for $Al(C_2H_5)_3 \cdot C_5H_5N$, 13.96% Al.

Pyridine was determined by distilling it from a highly alkaline solution, using a Kjeldahl distilling apparatus, into a measured amount of standard hydrochloric acid. The excess hydrochloric acid was determined by titration with standard base, using a pH meter. The equivalence point is difficult to determine even using this method. Found: 40.2% pyridine. Calculated for $Al(C_2H_5)_3 \cdot C_5H_5N$, 40.93% pyridine.

Results and Discussion. It thus appears that pyridine reacts with aluminum triethyl etherate to form $Al(C_2H_5)_3 \cdot C_5H_5N$ displacing the ether. From the data gathered, it is not possible to state whether the compound is formed by simple displacement of the diethyl ether by pyridine, driven by the higher basic strength and lower volatility of pyridine, or whether the aluminum triethyl has reacted with pyridine in a manner similar to the reaction of lithium ethyl with pyridine[46]:



However, lithium ethyl cleaves diethyl ether while aluminum triethyl forms a stable etherate so the behavior of the two compounds is not analogous. The more likely of the two reactions is the formation of a compound by displacement of the ether, with the nitrogen atom coordinated to the aluminum atom.

I. Additional Reactions of Aluminum Triethyl Etherate.

1. Reaction with Carbon Dioxide.

Procedure. The carbon dioxide was obtained from Dry Ice which was packed in a large Dewar flask with a stopper through which a T-tube was inserted. On one arm of the T-tube was a mercury seal and filter-paper pressure release disc and the other arm led to a drying tower, which was filled with phosphoric anhydride and sand. The reaction flask had an inlet tube which reached almost to the bottom of the flask. The outlet was protected by drying tubes.

The Dry Ice was allowed to sublime for several days in order to sweep the Dewar, drying tower and reaction flask free of air. Five ml. of aluminum triethyl were added to the reaction flask and carbon dioxide was allowed to bubble through the etherate for several days. In one run the reaction flask was equipped with a condenser and surrounded by an oil bath kept at 100°C. In all runs a small amount of solid formed around the inlet tube but most of the aluminum triethyl etherate seemed unchanged.

The reaction mixture was hydrolyzed, syrupy phosphoric acid was added, and the solution was distilled until only a viscous mass remained in the still pot. Some of the distillate was used to determine Duclaux constants[47] which were:

Acid	Fraction A	Fraction B	Fraction C
From carbon dioxide reaction	7.63	7.58	7.01
Acetic[47]	6.8	7.1	7.4
Propionic[47]	11.9	11.7	11.3

In order to estimate the equivalent weight, the distillate from the phosphoric acid was titrated with standard sodium hydroxide and the resulting solution evaporated to dryness, dried at 120-130°C., and weighed. The equivalent weight, thus determined, is 65.3. That of acetic acid is 60.05 and of propionic acid is 74.08. An attempt to make the p-bromophenacyl ester was unsuccessful. Some of the salt when acidified with sulfuric acid smelled strongly of acetic acid.

Results and Discussion. Aluminum triethyl etherate reacts only very slowly with dry carbon dioxide gas. Propionic acid and acetic acid appear to be formed on hydrolysis of the product. Propionic acid is the expected product from a Grignard-like addition of aluminum triethyl to carbon dioxide. No explanation can be offered for the formation of the acetic acid.

2. Reaction with Oxygen.

Procedure. Compressed air was dried and freed of carbon dioxide by passage through a tower filled with Ascarite, a gas-washing bottle of concentrated sulfuric acid, a tower containing a mixture of phosphoric anhydride and sand, and finally, another tower filled with Ascarite. The reaction flask was a three-neck flask, with a short inlet tube in one neck, a condenser in another neck and a stopper in the third neck. The outlet at the top of the condenser was protected with drying tubes. A magnetic stirrer was used.

The apparatus was swept out with dry, carbon dioxide-free air, the exit at the top of the condenser was closed, and a few ml. of aluminum triethyl etherate was introduced into the reaction flask. As the air came into contact with the etherate, considerable heat was given off and solid was formed. The air flow was continued for ten days. The white solid product still seemed to have some liquid on it which did not seem to be diminishing in amount with time. A sample was removed, hydrolyzed, and filtered. The filtrate gave a positive iodoform test. The flask and product were weighed, the flask was cooled in an ice bath and the reaction mixture was hydrolyzed. There was some effervescence when the water contacted the solid. The resulting slurry was stirred for several hours, then it was distilled and 100 ml. of distillate was collected. The specific gravity of the distillate was determined and, assuming that ethyl alcohol was the only volatile, water-soluble product, 2.8 g. of ethyl alcohol was obtained from 4.644 g. of reaction mixture. Calculated, if the product was pure $[Al(OC_2H_5)_3]_4$, 3.96 g.

Aluminum was determined on the reaction mixture by precipitation and weighing as the 8-hydroxyquinolate. Found: 19.49% Al. Calculated for $[Al(OC_2H_5)_3]_4$, 16.63% Al. Calculated for $Al(C_2H_5)_3 \cdot (C_2H_5)_2O$, 14.33% Al.

Results and Discussion. It is difficult to account for the high percentage of aluminum found in the product. However, only one run was made. It is possible that in the highly exothermic reaction that took place initially, some aluminum oxide and volatile products were formed. It is not possible to say what the products of this reaction are. It has been reported that zinc diethyl in petroleum ether solution precipitates a peroxide, $C_2H_5ZnOOC_2H_5$, when reacted with air[48]. This compound explodes on heating. Aluminum ethoxide may be formed or perhaps a peroxide analogous to that formed by zinc diethyl.

3. Reaction with Sulfur Trioxide.

Procedure. Sulfur trioxide vapor was obtained from liquid sulfur trioxide (Sulfan B, which contains a stabilizer). A distilling tube with T24/40 joints, containing a suction tube which extended approximately one inch below the end of the outer joint, and with a stopcock on the side arm, was to fit into the top of the sulfur trioxide bottle which has a T24/40 top. Into the upper end of this distilling tube a U-shaped tube, approximately 20 mm. in diameter, was fitted. The other end of this U-shaped tube was fitted into one neck of a three-necked flask. In another neck of the flask was a nitrogen outlet protected by drying tubes. Stirring was effected by means of a magnetic stirrer. The end of the distilling tube which was to fit into the top of the sulfur tioxide bottle was stoppered, the system was swept out with nitrogen, which entered through the side arm of the distilling tube, and a few ml. of aluminum triethyl etherate was added, in a current of nitrogen, through the third neck. The reaction flask was cooled with a Dry Ice-acetone bath, the stopper was removed from the bottom of the distilling tube and the sulfur trioxide bottle was quickly fitted on. The sulfur trioxide had a tendency to solidify on the cold walls of the flask. There was extensive charring in the reaction flask; in fact, the product appeared as a black and gray mass. The sulfur trioxide bottle was removed and the stopper on the distilling tube was replaced. The reaction flask was allowed to warm to room temperature, cooled in an ice bath, and hydrolyzed. The solution smelled of organic sulfur compounds. The solution was filtered and evaporated. The procedure of Shriner and Fuson[49], for the preparation of the thiuronium derivative of ethyl sulfonic acid (melting point 114.7°C.) was followed. This derivative was not obtained.

Results and Discussion. It was hoped, when this reaction was undertaken, that a sulfonic acid would be obtained. However, extensive charring could not be eliminated.

4. Reaction with Carbon Tetrachloride.

Procedure. In one run, carbon tetrachloride was added to aluminum triethyl etherate at room temperature. A vigorous reaction took place. The residue was hydrolyzed, acidified with nitric acid, and tested with silver nitrate. An abundant precipitate of silver chloride was formed. In another run, excess carbon tetrachloride was added to aluminum triethyl etherate which had been cooled to

-20°C. to -30°C. There was no evidence that any reaction took place. The reaction mixture was allowed to warm to room temperature and to stand overnight at room temperature. It was then cooled, hydrolyzed, acidified with nitric acid, and chloride was determined by precipitation and weighing as silver chloride. 4.1466 g. of aluminum triethyl etherate was used and 0.1320 g. of silver chloride was found. If the etherate had stripped out all the chlorine atoms, then 9.5 g. of silver chloride would have been formed.

Results and Discussion. The results of these two runs are not consistent enough to warrant drawing any further conclusion than that aluminum triethyl etherate has some tendency to remove chlorine atoms from carbon tetrachloride.

CHAPTER III. CONCLUSIONS AND SUMMARY.

A phase study has been made of the binary system aluminum triethyl-diethyl ether. The presence of a 1:1 compound with a freezing point of about -65.0°C. is indicated. The freezing point of the etherate has been determined directly as -64.0°C., and the freezing points of mixtures made by ether additions to the etherate show that it is a 1:1 compound. The analysis of the etherate for aluminum also indicates that it is a 1:1 compound. These results contradict the literature where it has been claimed that the etherate is $4Al(C_2H_5)_3 \cdot 3(C_2H_5)_2O$.

The reactions with aluminum triethyl etherate and the Lewis base, ethide ion in sodium ethyl and lithium ethyl, have been carried out and the products, sodium aluminum tetraethyl and lithium aluminum tetraethyl, have been isolated and analyzed. Sodium aluminum tetraethyl is a white crystalline solid melting around 125°C. Lithium aluminum tetraethyl forms white, rod-like crystals, melting around 160°C. with sublimation in a vacuum.

With sulfur dioxide, aluminum triethyl etherate gives aluminum ethyl sulfinate in almost quantitative yield. Aluminum ethyl sulfinate is a white, highly hygroscopic solid. Its identity was proved by analysis, by the preparation of the diethyl sulfone derivative and the disulfone derivative of ethyl sulfinic acid from it.

Aluminum triethyl etherate reacts with nitrogen dioxide to give a product, which when hydrolyzed yields N,N-diethylhydroxylamine. This compound was identified by its physical and chemical properties and by comparison of its infrared spectrum which is not in the literature, with the infrared spectrum of N,N-diethylhydroxylamine made by a known method.

With nitric oxide, aluminum triethyl etherate gives a product, which, when hydrolyzed, yields ethylnitrosohydroxylamine. This was identified by the analysis of its copper salt.

Pyridine reacts to form a 1:1 compound melting about -41°C. This compound was isolated and analyzed.

Aluminum triethyl etherate reacts very slowly with carbon dioxide giving small amounts of solid which when hydrolyzed yields propionic and acetic acids. With oxygen from dry air, aluminum triethyl etherate forms a white solid, which was not purified not identified. With sulfur trioxide extensive charring occurred. With carbon tetrachloride some chloride was formed.

It would appear from this study that in most reactions with simple inorganic compounds, aluminum triethyl etherate behaves in a manner similar to a Grignard reagent. The only exception was the extremely slow reaction with carbon dioxide. Aluminum triethyl etherate has several advantages over aluminum triethyl for synthetic work. It is much easier to prepare pure and in good yield, and the reactions involved in its preparation are easily controlled. Aluminum triethyl etherate is not as much of a hazard as aluminum triethyl since it does not ignite in air nearly as readily. The use of the etherate enables milder reactions, with fewer side reactions, than would be possible with aluminum triethyl, as, for example, with the oxidizing agent, dinitrogen tetroxide. The presence of the ether may promote reaction in some instances, as it does in Grignard reactions.

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I, Evelyn Ruth Blust Baker, was born in New Orleans, Louisiana, May 26, 1923. I received my secondary school education in the public schools of New Orleans. My undergraduate training was obtained at Newcomb College, Tulane University, from which I received the degree Bachelor of Arts in 1946. During the school year 1945-46, I was an undergraduate assistant in the Physics Department of Newcomb College and I held the same position in the Chemistry Department in 1946. In 1946 I was elected to Phi Beta Kappa.

I received the degree Master of Science from The Ohio State University in 1950. From 1946 to 1951 I held the position of Graduate Assistant in the Department of Chemistry. During Winter and Spring Quarters of 1952, I held a University Scholarship while working toward the degree Doctor of Philosophy.