

FORMATION AND ELECTROLYSIS OF DISUBSTITUTED
" ALKALI-METAL AMIDES

by

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I. INTRODUCTION

Study of the electrolysis of organic compounds began soon after the discovery of the electrolysis of water. Electroorganic chemistry attracted attention early in the nineteenth century. At that time it was known that many organic compounds conduct electricity, but no evidence of decomposition had been found. By 1830 detailed studies of different electrodes and a partial determination of gaseous products of electrolysis were being made. Electrolytic reactions were not used in synthesis, however, until 1847 when Kolbe discovered that aliphatic hydrocarbons could be prepared by the electrolysis of salts of aliphatic acids. Kolbe actually laid the foundations of electroorganic chemistry in 1849 when he made the first statement pertaining to the mechanism of electrolytic oxidation of the aliphatic acids. The field has expanded greatly since that time, and it is now possible to carry out syntheses by electrolytic reduction, oxidation, cathodic coupling, anodic coupling, and substitution.

Tetra-ethyl hydrazine, as well as hydrazines with higher alkyl substituents, has been synthesized. Tetra-methyl hydrazine has been prepared only with difficulty. None of the completely substituted hydrazines have been prepared by electrolytic coupling of the substituted amides. The specific problem is to attempt the preparation, particularly of the tetra-methyl hydrazine, by electrolysis of di-substituted alkali-metal amides in non-aqueous solvents.

The purpose of this investigation is to determine the products of the electrolysis of lithium dimethyl amide in non-aqueous solvents.

II. LITERATURE REVIEW

This section contains material concerning the preparation of disubstituted alkali-metal amides and the characteristics of substituted hydrazines that have been prepared chemically. The material was obtained from references, texts, and periodicals, which are parts of the published literature.

Preparation of Disubstituted Alkali-metal Amides from Organolithium Compounds

This section contains a description of the original method for the preparation of disubstituted alkali-metal amides, primarily a laboratory method⁽²³⁾, as refined by Gilman and co-workers⁽³⁷⁾. The method was originated by Schlenk and Holtz⁽⁵⁸⁾ and also by Ziegler and Colonius⁽⁷⁸⁾. The following paragraphs describe the preparation of reagents, procedures for the preparation of organolithium compounds, methods of analysis for organolithium compounds, and the reaction of organolithium compounds with amines.

Preparation of Reagents. The reagents employed in the preparations to be described could not be used as they were received from the chemical supply houses. They had to be purified, dried, and in the case of the alkali-metals brought to the proper size of particle.

Sodium, which may be obtained in one-pound blocks, can be cut into slivers and have the oxide removed with a good sharp knife. It

is advantageous to cut sodium while it is covered with a coat of clean, dry mineral oil to prevent further formation of oxide and hydroxide. Before the sodium is added to a reaction, the mineral oil can be removed by washing the sodium metal with petroleum ether. Sodium dispersions⁽⁴⁵⁾ may be prepared in the following manner.

Blocks of sodium metal are immersed in a dry, heavy hydrocarbon, such as toluene, xylene or mineral oil. The hydrocarbon must be inert to sodium, and it must have a boiling point which is higher than the melting point of sodium, 97.5 °C⁽⁵⁹⁾. The hydrocarbon, containing the sodium, is heated, and when the temperature approaches the melting point of sodium, the mixture is agitated vigorously. At a temperature of 100 °C the sodium will break up into small globules, the size of which depends upon the rapidity of the agitation. When the sodium particles attain the desired size, the mixture is cooled. Agitation may be stopped when the temperature of the mixture is below the melting point of sodium. If desired, the heavy hydrocarbon may be washed from the sodium particles with petroleum ether and may be replaced with suitable dispersing agents.

Several procedures⁽²⁸⁾ may be used for converting the small blocks of lithium, currently available, to the generally more effective smaller particles. With appropriate dies, the lithium metal can be pressed out in the forms of wires and ribbons of suitable shape and size. A rather sturdy press is necessary. Such wires and ribbons are not only readily cut into pieces which may be added directly into the reaction flask, but because of their uniformity their weight is readily determined, by measuring the length, after weighing a few of

the wires or ribbons to correlate length with weight. Such extruded shapes are conveniently stored in an inert solvent contained in stoppered Carius tubes. It is possible to prepare lithium powder after the procedure described above for sodium dispersions. In ordinary cases, lithium in this fine state is unnecessary. Furthermore, the rate of formation of lithium nitride, when nitrogen is used as the inert atmosphere, is noticeably increased with very finely divided lithium. Fine lithium may also be prepared by means of a rasp, the particles being added directly from a weighed block of the lithium. This procedure is rather tedious and time consuming for moderately sized preparation, and tends to cause the inclusion of a considerable amount of oxidized lithium in the reaction. A convenient procedure is to hammer the lithium, wet with benzene or toluene, into a thin sheet on an anvil. This is preferably done in a hood, because lithium oxide dust is irritating to the nose and throat. The thin sheet, about a millimeter in thickness, is then cut into strips one to three millimeters wide, and these are then cut with scissors into the reaction flask, through a paper funnel in the neck of the flask and in an emerging stream of nitrogen. The lithium prepared in this manner has a large, oxide-free surface and is suitable for reaction with most organic halides.

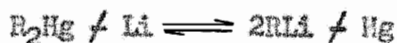
Diethyl ether may be dried by two different methods. The first method consists of placing a small amount of sodium hydride into the ether. The mixture is mildly agitated for about three minutes and then allowed to stand for several hours with occasional mild agitation until all bubbling has ceased. The dry ether is then decanted from the

solid residue, containing sodium hydride and sodium hydroxide. The decanted ether is then distilled but not to dryness. Petroleum ether may be dried in the same manner. The second method^(10,11) consists of placing the ether to be dried over concentrated sulfuric acid. The heat generated, as the acid removes water from the ether, will distill the dry ether from the acid. The concentrated sulfuric acid does not remove only water, but also unsaturated compounds formed by decomposition of the ether.

For the preparation of crystalline ethyllithium "Anala R" benzene was purified by fractional freezing, this process was repeated five times, and gave material n_D^{20} 1.5010, which solidified to a clear glass at 5 °C. n-Pentane was freed from unsaturated and aromatic compounds by several hours shaking with five per cent oleum, then washed, dried, and distilled over sodium. The fraction boiling point 35 to 36 °C was used. All alkyl halides had a boiling point range of less than 0.5 °C.

General Procedure for the Preparation of Organolithium Compounds.

Organolithium compounds were first prepared by Schlenk and Holtz⁽⁵⁸⁾ by the reaction of lithium with an R_2Hg compound in accordance with this general reaction which has been shown to be reversible^(42,62,71,78).



The technique in this operation was subsequently improved and excellent yields of alkyl lithium compounds were obtained more conveniently^(43,44). More recently the studies by Ziegler and Colonius⁽⁷⁸⁾ have shown that it is possible to prepare many organolithium compounds by the direct interaction of lithium with an alkyl halide in ether or

benzene, the latter solvent being preferred with alkyllithium compounds, because they react much more rapidly with ether than do aryl lithium compounds.



Schlenk^(37,38) tubes are unnecessary and the preparations are conveniently carried out in the conventional three-necked, round-bottom flasks fitted with a mercury-sealed stirrer, reflux condenser, and dropping funnel. An inert atmosphere of dry nitrogen, free of oxygen and carbon dioxide, is used in the preparation and subsequent reaction of the organolithium compound. As is the case with Grignard preparations, which were developed previously, the halide is added at a rate to maintain gentle refluxing. With those organic halides which react slowly and which show no appreciable drop in yield with rapid addition, the organic halide is added at one time^(27,36,37,38). In the preparation of some organolithium compounds which require a relatively long time for completion, there is the probability of using up some of the lithium and also the possibility of subsequent secondary reactions by the fairly rapid formation of lithium nitride. In these and other special cases, it may be desirable at times to use another inert atmosphere with only occasional escape of inert gas^(27,36,37,38) or by a trap for carrying out reactions in an inert atmosphere⁽²⁵⁾.

Glass sealed containers of various modifications^(37,38) have been used for the preparation and subsequent reaction of the organoalkali compounds, to exclude completely the damaging effects of the atmosphere

and moisture. Comparison with the preparation of Grignard reagents indicates glass-sealed containers are not necessary, and that simpler methods may be used for the preparation of organoalkali compounds.

This finds support in experiment. Phenyllithium can be prepared very readily and in excellent yields from lithium and bromobenzene in ether. The general procedure is that postulated above. Actually, the 95 per cent yield of phenyllithium is 15 to 25 per cent in excess of that reported previously^(42,62,71,78). As a check on the analytical procedure the phenyllithium was treated with an equivalent of benzophenone and the yield of triphenylcarbinol obtained in this manner was essentially that expected. For this reason, it was considered unnecessary to use also the n-butyl bromide - dibenzyl mercury indirect method of analysis^(42,62,71,78).

It might be predicted that the rapid addition of n-butyl chloride to lithium would not decrease the yield, because it did not occur in the similar preparation of the related Grignard reagent. This prediction is supported by experiment, and there is no essential drop in yield with the rapid addition of n-butyl chloride to lithium in ether. The reaction between n-butyl chloride and lithium in benzene is slow^(42,62,71,78) and the yield of n-butyllithium after six hours is 70 per cent. However, the formation of n-butyllithium in ether is more rapid and yields of 75 to 80 per cent are readily obtained.

The practical significance of the observation that there is no appreciable drop in yields in the preparation of phenyllithium and n-butyllithium lies in the fact that these organolithium compounds

can be prepared conveniently without regard to the rate of addition of halide. If analogies between organometallic compounds prepared from alkali metals and alkaline earth metals have any significance, then it is that the yields of other organolithium compounds will vary with the rate of addition. An excess of lithium has no effect on the yields of organolithium compounds mentioned here^(62,78).

The advantages of manipulating organolithium compounds in either open containers or with a slow stream of nitrogen in low pressure containers provided with the conventional mercury-sealed stirrer should apply with other organoalkali compounds.

Carbon dioxide, one of the atmospheric constituents that has a destructive effect on reactive organometallic compounds, reacts with phenyllithium to give a very poor yield^(42,62,71,78) of benzoic acid. Oxygen with phenyllithium induces chemiluminescence. Due to this phenomena, the color tests^(31,32,34,35), developed by Gilman, for reactive organometallic compounds, have been found to be useful to determine whether an organolithium compound has been formed.

The Yields of Some Organolithium Compounds. The general analytical procedure is described later in this literature review. Alterations introduced in the manipulations correspond with those described previously. First, the Schlenk or Carius tubes are unnecessary. It is sufficient to remove the oxide coating from the lithium by scraping and then washing the metal with dry ether. Second, the lithium can be cut in many fine pieces by sharp bandage scissors of short blade length and long handles. These small pieces

of lithium remain relatively untarnished, if there is a rapid stream of inert, dry nitrogen, from the reaction vessel.

The results given in Tables I, II, III, and IV on pages 11, 12, 13, and 14 respectively, are those obtained under three sets of conditions⁽³⁸⁾. In the first or "a" condition 0.05 mol. of RX compound is used, 40 drops (or 0.3 to 0.4 gram of the solid halide) being used to start the reaction and the remainder in 15 milliliters of dry ether is added over a period of 30 to 35 minutes, about a drop every second. The 0.76 gram (0.11 atom) of lithium cut into 30 to 32 pieces is added to 15 milliliters of ether contained in a graduated reaction flask. Accordingly, the total volume of ether used is 30 milliliters or 0.3 mol. The mixture is stirred at the outset and heat is applied externally at the beginning and later also if the heat of reaction is insufficient to cause gentle refluxing. Stirring and refluxing are continued for an hour. The diluent, ether or benzene, is added to bring the solution to a volume of 100 milliliters and then, after a few minutes of stirring to obtain a homogeneous solution, the flask is detached and allowed to stand for 30 minutes. After this time, samples are removed for titration.

The second or "b" conditions are essentially those used to determine the drop in yield, when the halide is added at once in 15 milliliters of dry ether to the cut lithium, heat being applied externally until the reaction starts, which is usually one-half to one minute.

The third or "c" conditions differ from the "a" conditions only in the degree of fineness of the lithium, the 0.76 gram being cut into 165 to 170 rather than 30 to 32 pieces.

TABLE I

Yields of Some Alkylolithium Compounds

| Halide | Yield ^a % | Yield ^b % | Yield ^c % |
|---|-------------------------|-------------------------|-------------------------|
| CH ₃ I | 73.6 ^d | 65.5 | 81.5 |
| n-C ₄ H ₉ Cl | 76.1 | 67.5 ^e | 77.1 |
| n-C ₄ H ₉ Br | 59.0 ^f | 42.8 | 68.8 ^g |
| n-C ₁₁ H ₁₂ Br | 38.5 | 30.2 | ^h |
| cyclo-C ₆ H ₁₁ Cl | 23.0 | 19.0 ⁱ | 24.3 |

^a Halide was added over a period of 30 minutes.

^b Halide was added entirely at the start of the reaction.

^c Lithium, 0.76 gram, was added in 165 to 170 pieces instead of 30 to 32.

^d The yield is less with methyl iodide from unsealed containers. Freshly distilled methyl iodide, or methyl iodide from sealed containers is recommended. Refluxing 15, 30 or 45 minutes gives about the same yield. A yield of 82 per cent was obtained under "a" conditions with 0.1 atom of lithium and 0.125 mol of methyl iodide. Methylolithium has been prepared from methyl chloride or bromide using methyl iodide as a catalyst. The "a" conditions with 10-12 molecular equivalents of ether will give yields as high as those described in the "c" conditions. It is significant that methylolithium is stable in ether.

^e The "drop yields" are inclined here to be erratic, and the 67.5 per cent is a minimum yield.

^f The yield is markedly decreased without stirring, dropping in some cases to 10.5 per cent.

^g The finely cut lithium in the n-butyl bromide and methyl iodide experiments tends to aggregate into a single mass. However, when this does happen, it is apparently without any significant effect on the yield.

^h No experiment was made with very fine lithium.

ⁱ A reaction takes place with cyclohexyl bromide, but no appreciable quantity of organolithium compound was formed.

Gilman, H., E. A. Zoellner and W. M. Selby: Yields of Some Organolithium Compounds by the Improved Procedure, J. Am. Chem. Soc., 55, 1252 (1933).

TABLE II

Yields of Some Aryllithium Compounds

| Halide | Yield ^a | Yield ^b | Yield ^c |
|-------------------------------------|--------------------|--------------------|--------------------|
| | % | % | % |
| C ₆ H ₅ Cl | 35.4 ^d | 35.0 | 48.7 |
| C ₆ H ₅ Br | 95.2 ^e | 91.1 | 97.5 ^f |
| C ₆ H ₅ I | 80.1 | 80.7 | 82.8 |
| α-C ₁₀ H ₇ Br | 79.0 ^g | 82.4 | 96.0 |
| β-C ₁₀ H ₇ Br | 74.0 | 76.3 | 83.1 |

^a Halide was added over a period of 30 minutes.

^b Halide was added entirely at the start of the reaction.

^c Lithium, 0.76 gram, was added in 165 to 170 pieces instead of 30 to 32.

^d Occasional erratic yields with chlorobenzene may be due to varying coatings with lithium chloride. To reduce the coating effect of lithium chloride, the lithium was added in three separate portions with refluxing for one hour after each addition. The yield was 51.2 per cent. The yield was 52 per cent when a steel stirrer with knife edge was used to remove the coating partially; and with 310 pieces of lithium and refluxing for 1.25 hours, the yield was 53.5 per cent and the solution was light yellow in color.

^e The yield is 96.2 per cent when the halide is added over one hour rather than 30 minutes. However, with 10 instead of six equivalents of ether the yield is 98.5 per cent, and this is due in part to the lesser precipitation of lithium bromide. There is no improvement when the halide is added more slowly. No experiment with intermediate quantities of ether were tried. When more than six equivalents of ether are used it is recommended that three be used to dilute the halide and the rest be added initially to the lithium.

^f With the fine pieces of lithium used under these conditions there is no drop in yield when the bromobenzene is added at one time.

^g On standing for a moderate time there was no separation in the ether solution. The organolithium compound in an ether - benzene solution has an opaque purple color.

Gilman, H., E. A. Zoellner and W. M. Selby: Yields of Some Organolithium Compounds by the Improved Procedure, *J. Am. Chem. Soc.*, **55**, 1252 (1933).

TABLE III

Yields of Some Toluylithium Compounds

| Halide | Yield ^a % | Yield ^b % | Yield ^c % |
|--|-------------------------|-------------------------|-------------------------|
| o-CH ₃ C ₆ H ₄ Br | 93.3 | 85.6 | 97.0 ^d |
| m-CH ₃ C ₆ H ₄ Br | 85.1 | 85.0 | 93.7 ^e |
| p-CH ₃ C ₆ H ₄ Br | 97.6 | 95.6 | 99.2 |
| 1,4,2 (CH ₃) [(CH ₃) ₂ CH] C ₆ H ₃ Br | 74.0 | 69.2 | 90.0 ^f |

^a Halide was added over a period of 30 minutes.

^b Halide was added entirely at the start of the reaction.

^c Lithium, 0.76 gram, was added in 165 to 170 pieces instead of 30 to 32.

^d Addition of o-bromotoluene at one time, under these conditions, gives a 95 per cent yield. The already high yield was not increased with 10 equivalents of ether.

^e Spontaneous refluxing ceased after 20 minutes, and at the same time the solution started to deposit lithium bromide. As in the other related cases, external heat was then applied so that gentle refluxing was maintained throughout the preparation. The yield under "c" conditions are erratic at times. In the present case one yield of 88 per cent was noted. The difficulty may be due to the varying agglomeration of the finely cut lithium. Check results within two per cent are obtainable with the "a" and "b" conditions. With 10 molecular equivalents of ether, instead of six, under "a" conditions, the yield is 98.8 per cent.

^f The very fine cut lithium is unnecessary for high yields because 10-12 equivalents of ether in the "a" conditions also gave a 90 per cent yield.

Gilman, H., E. A. Zoellner and W. M. Selby: The Yields of Some Organolithium Compounds by the Improved Procedure, J. Am. Chem. Soc., 55, 1252 (1933).

TABLE IV

Yields of Some Substituted Aryllithium Compounds

| Halide | Yield ^a % | Yield ^b % | Yield ^c % |
|---|-------------------------|-------------------------|-------------------------|
| o-CH ₃ OC ₆ H ₄ Br | 84.2 | 86.0 | 87.9 |
| p-CH ₃ OC ₆ H ₄ Br | 75.4 | 66.0 | 87.9 ^d |
| o-C ₂ H ₅ OC ₆ H ₄ Br | 73.0 ^e | 75.2 | 82.6 |
| p-C ₂ H ₅ OC ₆ H ₄ Br | 76.7 ^e | 76.3 | 92.7 |
| p-(CH ₃) ₂ NC ₆ H ₄ Br | 94.8 ^f | 95.0 | 96.1 |
| p-C ₆ H ₅ C ₆ H ₄ Br | 76.7 ^g | 73.9 | 81.5 |

^a Halide was added over a period of 30 minutes.

^b Halide was added entirely at the start of the reaction.

^c Lithium, 0.76 gram, was added in 165 to 170 pieces instead of 30 to 32.

^d This experiment emphasizes the desirability of continuous refluxing throughout the preparation. If external heat is applied after the spontaneous heat of reaction has subsided, the yield is significantly decreased even though the time interval is brief. This may be due to the partial deposition of lithium halide which is subsequently removed with difficulty. Fine lithium is unnecessary, for the yield under "a" conditions with 12 equivalents of ether is 93 per cent, and with 14 equivalents somewhat less.

^e The effect of more ether was not studied, but it is probable that 10-12 equivalents of ether will give yields in excess of 90 per cent.

^f The high yield of p-dimethylaminophenyllithium irrespective of the rate of addition of halide or fineness of lithium suggested extra confirmation. The unused lithium was assembled and shown to correspond with the high titration values. Austin in his description of this preparation⁽⁸⁵⁾ mentions the difficulty of titration because of the colored solutions.

^g Reaction set in at once. A slightly larger than usual quantity of ether was used. The solution of organolithium compound is dark blue in color.

Gilman, H., E. A. Zoellner and W. M. Selby: The Yields of Some Organolithium Compounds by the Improved Procedure, *J. Am. Chem. Soc.*, 55, 1252 (1933).

Petroleum Ether as a Solvent. Petroleum ether, boiling point 28 to 38 °C, is peculiarly suitable⁽²⁸⁾ for the preparation of some organolithium compounds, particularly when solutions are to be stored or when special solvents are used later to replace most of the petroleum ether. The rate of formation of n-butyllithium in petroleum ether approaches that in diethyl ether and n-butyl chloride is really more effective in petroleum ether than in diethyl ether. Four particular advantages of petroleum ether may be stated:

1. The difficulty of secondary reactions like cleavage, which can and usually does occur in diethyl ether, is removed.

2. Indirect supplementary analyses⁽⁷⁸⁾ are not necessary to determine the titer of solution, and the simple acid titration analysis⁽³³⁾ is sufficient.

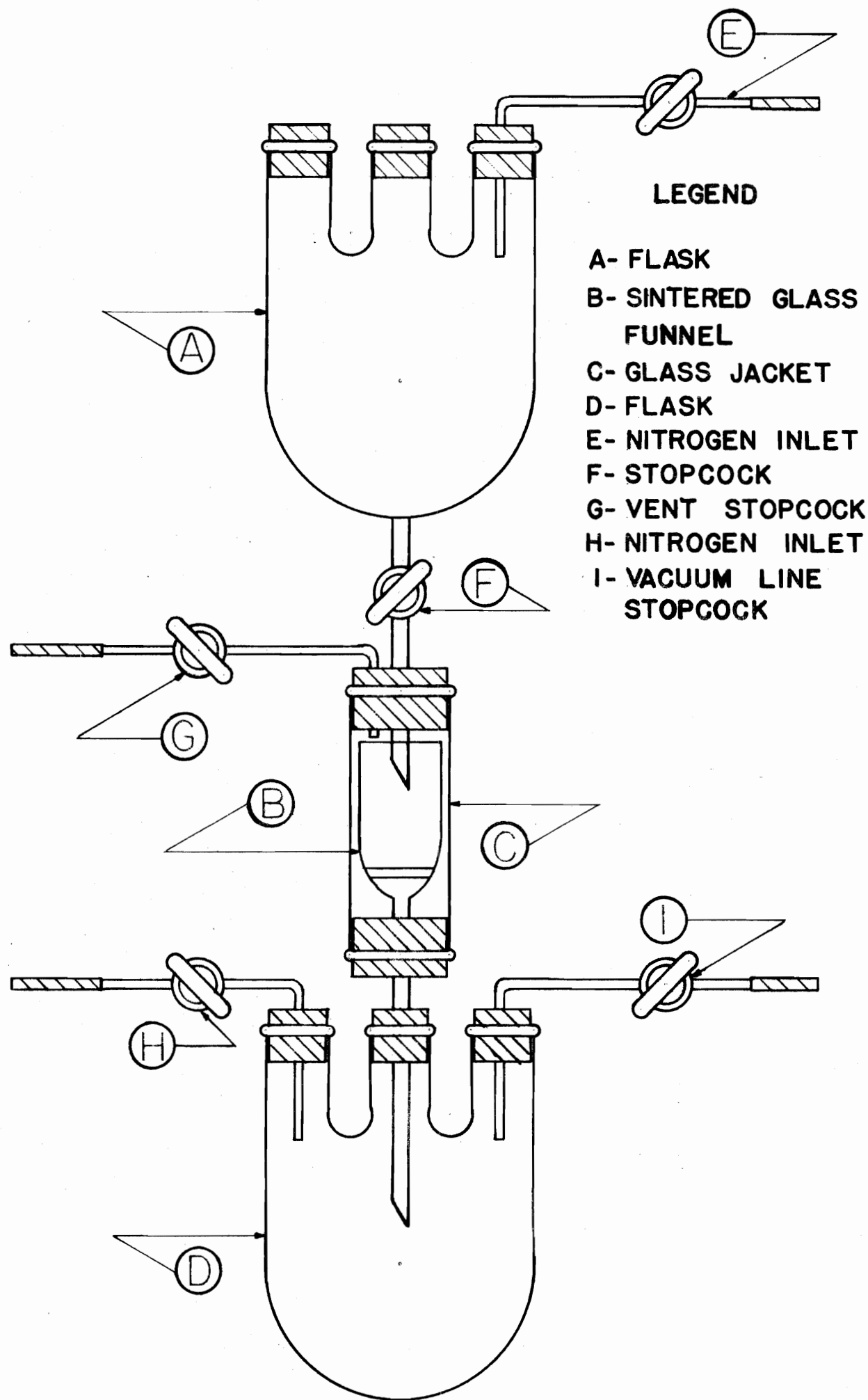
3. The byproducts, like lithium halide, are insoluble in petroleum ether and may be removed by filtration. Some of these filtered solutions have been kept for extended periods with no significant change. Some higher boiling fractions of petroleum ether appear to be less satisfactory.

4. Isopropylolithium is obtainable in 58 per cent yield from isopropyl chloride, but only in petroleum ether. It was not possible, at first, to prepare isopropylolithium directly⁽⁸⁰⁾. Later it was obtained by the direct reaction of isopropyl chloride and lithium in only a 20 per cent yield⁽³⁹⁾. The yield of some other organolithium compounds prepared in petroleum ether are 50 per cent ethyllithium from ethyl bromide, 60 per cent

n-propyllithium from n-propyl bromide, 70 per cent n-butyllithium from the bromide, and 75 per cent from the chloride.

Filtration of Organolithium Compounds. There are three general ways⁽²⁸⁾ of handling organolithium solutions prior to mixing with a reactant. First, no filtration of the organolithium solution from particles of unused lithium, lithium halide, oxide, carbonate, and nitride may be needed for some reactions. Second, a rough separation may be adequate, and this can be done either by allowing the solid matter to settle and then decanting or by filtration through loosely packed glass wool, asbestos or similar material. In this latter procedure the solution is poured through a glass tube connected with a gooch adapter, containing glass wool, held in one neck of another three-necked flask previously fitted with a condenser and stirrer. By means of a T-tube a single stream of dry nitrogen provides an inert atmosphere for both flasks.

Third, a fine filtration may be accomplished by the use of appropriate filter disks, sticks, or funnels. This can be done in an apparatus provided with interchangeable ground joints or in a more accessible apparatus fitted with rubber stoppers. Figure 1 on page 17 illustrates the essential features of an apparatus of this type⁽⁴¹⁾. The solution to be filtered is transferred under nitrogen to flask A, which is a standard three-necked flask, to the bottom of which has been sealed a stopcock of fairly large bore, two to four millimeters. Flask A provided with an inlet tube E, for nitrogen, empties into the sintered glass funnel, B, enclosed in the glass jacket, C.



LEGEND

- A- FLASK
- B- SINTERED GLASS FUNNEL
- C- GLASS JACKET
- D- FLASK
- E- NITROGEN INLET
- F- STOPCOCK
- G- VENT STOPCOCK
- H- NITROGEN INLET
- I- VACUUM LINE STOPCOCK

GRAHAM, E. AND G. CALINGAERT: DETERMINATION OF SULFUR IN GASOLINE, IND. ENG. CHEM., ANAL. ED., 2, 104 (1930)

FIGURE I. FILTRATION APPARATUS FOR ORGANOLITHIUM COMPOUNDS

The original solution of organolithium compound is allowed to settle, transferred to flask A and then flask A is stoppered. The nitrogen inlet, H, on flask, D, is closed by a stopcock or screw clamp, and a slightly reduced pressure is caused by opening stopcock, I, to a water pump which has between it and stopcock, I, a drying tower and traps. Then stopcock, F, is opened to permit enough solution to run into funnel, B, to partially fill it. A special tube can replace both B and C if it is available. Stopcock, G, is useful for relieving excess back pressure due to vaporization of low boiling solvents. The filtration rate is rapid, and by means of a sintered glass funnel of moderate porosity, 20 to 30 microns, Schott Jena - G-3 has been found most satisfactory, one-half liter of solution was filtered in 15 minutes. Strong suction should not be applied at I, particularly with low boiling solvents. A preliminary settling of the initial reaction mixture is recommended in order not to clog the filter unduly. The filtrate was uncommonly clear not only with organolithium compounds but also with other organometallic compounds like some highly turbid organoaluminum halides. The filtered solution can be used directly, or can be stored in suitable graduated containers from which aliquots may be removed as desired from time to time.

Preparation of Ethyllithium in the Crystalline State. Pure crystalline ethyllithium was obtained⁽⁶⁵⁾ by the reaction of lithium with ethyl bromide and separation from lithium bromide by differential solubility in benzene and hexene or isopentene. All experiments were made in pure nitrogen since the product is flammable in air.

To 3.8 grams of lithium slices in 200 milliliters of isopentene was added slowly 21.8 grams of ethyl bromide, usually the reaction started spontaneously after 0.3 to 2 hours and the mixture became opaque and acquired a grey or violet color. After the addition (3.5 hours) the mixture was refluxed 1.5 to 2 hours to complete the reaction. The mixture was diluted with 11 to 200 milliliters of benzene and warmed to 35 °C. Most of the isopentene was distilled off with stirring. The remaining mixture was siphoned into a settling vessel, a buret with the stopcock located somewhat above the bottom, thus providing a settling chamber for the precipitate, in which a clear solution of ethyllithium in benzene was obtained after 12 to 14 hours. The yield of ethyllithium was about 65 per cent. The clear solution was transferred to a three-necked flask. Some 50 to 60 milliliters of benzene were distilled off, and the residue was treated with 20 milliliters of dry isopentene. The mixture was chilled with ice and sodium chloride, and the crystals were filtered by suction and nitrogen pressure. They were then washed with dry pentene, and dried at 40 to 50 °C.

The product, ethyllithium, forms a colorless crystal powder, decomposes at 95 °C, and it can be recrystallized from hexane. It is soluble in hot benzene and hexane, readily forming supersaturated solutions; the solubility in grams per 100 grams solution in pentane is 1.0 at 18 °C, in isopentene, 3.0 at 16 °C and 2.0 at 0 °C, in hexane, 9.5 at 55 °C and 6.0 at 18 °C and in benzene 7.0 at 16 °C. Ethyllithium has a low solubility in n-pentane and in this case portions

of the stirred suspension were removed for estimation. It was found that the solubility of ethyllithium in n-pentane is 7.6 grams per liter at 20 °C.

A similar preparation in pentane gave only 10 to 20 per cent yield, while the above procedure gave 33 to 35 per cent.

An alternate procedure⁽⁶⁵⁾ was as follows. To four grams of sliced lithium in 130 milliliters of absolute ether was added gradually 21.8 grams of ethyl bromide, with ice cooling, since the reaction is very vigorous. After completion of reaction, 120 milliliters of benzene were added and the ether was distilled off, with stirring. The dark solution gradually deposited a colorless precipitate as the ether was removed. When the warm solution was allowed to settle after concentration, it yielded a precipitate of 10:7 ethyllithium to lithium bromide. The filtrate contained these in a 7:1 ratio. Separation of pure ethyllithium by this method is impossible. For analysis the samples were ampuled under nitrogen. The ampules were broken under benzene and in a nitrogen atmosphere, treated with five milliliters of absolute ethyl alcohol, then with 50 to 100 milliliters of water and titrated with standard acid.

The Preparation of Isopropyllithium. One manipulation of organolithium compounds of particular interest is the exclusive use of low boiling petroleum ether for the preparation of organolithium compounds. Not only is petroleum ether of value in some preferential reactions but it also makes it possible to obtain some organolithium compounds previously prepared with difficulty and in low yields.

One of these is isopropyl lithium, which could not be directly prepared at first⁽⁸⁰⁾ and which was later obtained by the direct action of isopropyl chloride and lithium in only a 20 per cent yield⁽³⁹⁾. In low boiling petroleum ether⁽⁸⁸⁾, 13.2 grams isopropyl chloride react smoothly with 3.8 grams of lithium to give isopropyl lithium in 58 per cent yield. As described previously, the reaction must be carried out in an inert atmosphere of dry nitrogen.

The Preparation of n-Butyllithium. The method of preparation of n-butyllithium commonly used until recently gave from 50 to 65 per cent yields in 90 minutes in diethyl ether as determined by the double titration method⁽²⁴⁾. A study of the reaction⁽²¹⁾ at lower temperatures has revealed that yields of 75 to 90 per cent can be consistently obtained at about -10°C using n-butyl bromide with diethyl ether as the solvent. Only conventional apparatus is needed, and the reaction is substantially complete in 90 minutes. Table V on page 22 gives data on several preparations made under varying conditions. n-Propyl, n-amyl, and n-hexyl bromides gave by this procedure 78, 81, and 77 per cent yields respectively of the corresponding lithium compounds.

The following is a description of a typical preparation which may be used to prepare n-butyllithium. Into a 500-milliliter three-necked flask, equipped with a stirrer, low temperature thermometer, and a dropping funnel, was placed 200 milliliters of ether dried over sodium. After sweeping the apparatus with dry, oxygen-free, nitrogen, 8.6 grams (1.23 gram atoms) of lithium wire, weighing 4.2

TABLE V

Preparation of *n*-Butyllithium

| Run No | Time of Addition | Temperature of Addition | Type of Lithium | Lithium Used | <i>n</i> -Butyl Bromide | Final Con- centration | Yield ^a | Stirring after Addition |
|--------|------------------|-------------------------|-------------------|--------------|-------------------------|--------------------------|--------------------|----------------------------|
| | min | °C | | gm atom | mol | molar | % | hr |
| 1 | 30 | -20 | cut ^b | 2.2 | 1.0 | 0.835 | 77.7 | 1.25 |
| 2 | 25 | -5 | cut | 1.0 | 0.5 | 1.20 | 82.9 | 1.0 |
| 3 | 35 | 0 | sand ^c | 1.0 | 0.5 | 1.47 | 77.3 | 2.0 |
| 4 | 35 | -10 | cut | 1.14 | 0.5 | 1.25 | 85.4 ^d | 2.0 |
| 5 | 35 | -10 | wire | 1.23 | 0.5 | 1.14 | 83.7 ^e | 2.0 |
| 6 | 15 | -10 | cut | 3.3 | 1.5 | 0.89 | 80.0 | 3.0 |

^a Yield after filtration was determined by double-titration.

^b Prepared as described on page 5.

^c Supplied by the Metalloy Corp., Minneapolis, Minn.

^d In this run helium was used instead of nitrogen and double-titrations were made five minutes, one hour, and two hours after addition, yields were 78.5, 83.9, and 85.4 respectively.

^e Yield determined by double-titration before filtration was 90 per cent; the above yield was determined after storing 16 hours at 10 °C following filtration.

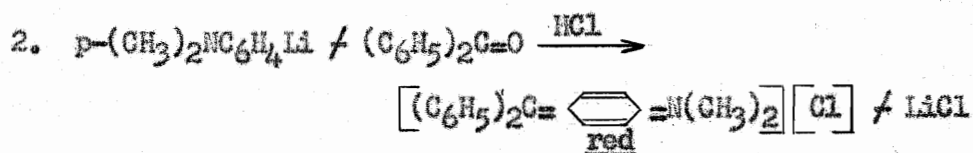
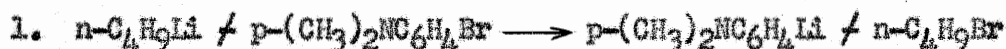
Gilman, H., J. A. Beel, C. G. Brannen, M. W. Bullock, C. E. Dunn, and L. S. Miller: The Preparation of *n*-Butyllithium, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

to 4.3 grams per meter, was wound in a loose coil, rinsed with ether, and the flattened coil was cut into pieces about seven millimeters in length which fell directly into the reaction flask in a stream of nitrogen. With the stirrer started, about 30 drops of a solution of 68.5 grams (0.5 mol.) n-butyl bromide in 100 milliliters of ether was added from the dropping funnel and the reaction mixture was then cooled to -10°C with a dry ice - acetone bath kept at approximately -30 to -40°C . The solution becomes slightly cloudy and bright spots appear on the lithium when the reaction has started. The remainder of the n-butyl bromide solution was then added at an even rate over a 30-minute period while maintaining the internal temperature at -10°C . After the addition was complete, the reaction mixture was allowed to warm up to 0 to 10°C while stirring for one to two hours. The reaction mixture was then filtered by decanting through a narrow tube plugged with glass wool into a graduated dropping funnel previously flushed with nitrogen. The yield determined by double titration⁽²⁴⁾ was 90 per cent before filtration and 83 per cent after filtration and storing 16 hours at 10°C . After four days at 10°C the yield was 82.5 per cent.

Methods for Qualitative Analysis of Alkylolithium Compounds.

The first analytical method described here was developed by Gilman⁽³²⁾ and designated as, "Color Test A". One-half to one milliliter of the organometallic solution was added to an equal volume of a 15 per cent solution of p-bromodimethyl aniline in dry benzene. Then one milliliter of a 15 per cent solution of benzophenone in dry benzene was

added, and after a few seconds the mixture was hydrolyzed with water and acidified with concentrated hydrochloric acid. A red color in the water layer is a positive test for a reactive organolithium compound. The reactions involved with n-butyllithium are as follows:



Some limitations of this test are as follows. It should respond to all organometallic compounds that can cause a fairly prompt halogen-metal interconversion with p-bromodimethylaniline. There are, however, significant differences among the alkyllithium compounds. As mentioned by Gilman^(20,30), the order of decreasing effectiveness of some alkyllithium compounds in the halogen-metal interconversion reaction with α -bromonaphthalene is: n-propyl, ethyl, butyl, phenyl, and methyl. In general, it appears that all alkyllithium compounds with the exception of methyllithium and the ethynyllithium compounds like phenylethynyllithium will give positive results with this test.

Another test developed by Gilman, supplements color test I⁽³¹⁾, II⁽³²⁾, and III⁽³⁵⁾, which primarily concern alkylmagnesium halide compounds. Like test II, the present test, numbered IV⁽³⁴⁾ by Gilman, can be used to differentiate alkyllithium compounds from alkylmagnesium halide compounds, but in a more effective manner for

two reasons. First, it is more comprehensive as it gives prompt colors with phenyllithium and methyllithium, which the test A described above will not do. Also methyllithium will not give positive results with test II. Second, it is more sensitive than test II and only slightly less sensitive than the widely applicable test I which uses Michler ketone.

The color test was carried out by adding one milliliter of the organometallic solution, without shaking, to 0.5 milliliter of an approximately molar solution of benzylamine in unsaturate free, dry petroleum ether, boiling range 60 to 68 °C was generally used. The appearance of a cherry red color in a few seconds is a positive test. If the organometallic solution is rather dilute, the color may fade in a few minutes. The shade of the red color depends to some extent on the concentration of the organometallic solution.

Methods for Quantitative Analysis of Alkylolithium Compounds. The simple acid titration procedure⁽³³⁾ for the quantitative analysis of organometallic compounds which give bases on decomposition by water, yields values that may be high particularly with organometallic compounds which cleave ether. For example, the lithium hydroxide formed by hydrolysis of an aliquot of an organolithium compound is derived not only from the organolithium compound but from alkoxy-lithium compound, as well as from lithium hydroxide and lithium oxide due to traces of water and oxygen.

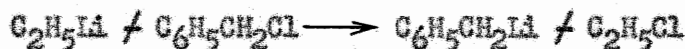
Ziegler and coworkers⁽⁷⁹⁾ obtained true titration values by a differential based on titration of two aliquots. One titration was

for the total lithium hydroxide present. The other titration was for the lithium hydroxide present after destroying the alkyllithium compound, and the difference between the two titrations gave the quantity of alkyllithium compound. Prior to the second titration the alkyllithium compound was destroyed by adding n-butyl bromide and dibenzylmercury. The benzyllithium formed by reaction of the organolithium compound and dibenzylmercury was promptly decomposed by the n-butyl bromide.

It was found that benzyl chloride is a more convenient reagent than the n-butyl bromide - dibenzylmercury combination for removing the alkyllithium compound. The reaction which occurred appears to be similar to that observed earlier by Späth⁽⁶¹⁾ and by Fuson^(14,19) with Grignard reagents, three coupling products being formed:



The above overall reaction was not a complete picture of the transformation involved. Benzyllithium is an intermediate compound formed as the consequence of a halogen - metal interconversion reaction^(24,26):



The benzyllithium formed in this manner undoubtedly accounts for part of the bibenzyl by a coupling reaction with some of the benzylchloride. The transitory yellow color observed when benzyl chloride is added to n-butyl lithium was due to the benzyllithium. More

particularly, the benzyl lithium was captured as phenylacetic acid when a mixture of ethyllithium and benzyl chloride, cooled to -50°C to reduce the rate of coupling, was very rapidly carbonated by solid carbon dioxide.

The quantitative analysis procedure is applicable to alkyllithium but not to aryllithium compounds. It cannot be used with methyllithium and with phenylethynyllithium, because of their lesser activity.

The solution of an alkyllithium compound was filtered⁽²⁸⁾ under nitrogen, preferably through a sintered glass funnel, to remove insoluble material. An aliquot of five or 10 milliliters was withdrawn, by means of a rubber suction bulb connected to a pipet, and hydrolyzed in 10 milliliters of distilled water. Titration with standard acid, using phenolphthalein as an indicator, gave the total alkali. Another five or 10 milliliters aliquot was added to 10 milliliters of dry ether containing one milliliter of benzyl chloride. The benzyl chloride was purified by drying over phosphorus pentoxide and then distilling at reduced pressure. As the alkyllithium solution was dropped into the benzyl chloride, as rapidly as it drained from the pipet, a yellow color flashed through the liquid. If the alkyllithium solution was concentrated, a white precipitate of lithium chloride formed with the disappearance of the yellow color. The ether solution might become warm enough to boil, but it was not cooled. The mixture was allowed to stand one minute after the addition, then hydrolyzed, and titrated with standard acid. Care must be taken not to overstep the end point in this titration since the aqueous

layer decolorizes before the ether layer. This may be overcome by vigorous shaking near the end point.

The benzyl chloride must be dissolved in ether because coupling with alkyllithium compounds takes place much less readily in other solvents. In analyses of organolithium compounds prepared in petroleum ether, the benzyl chloride should be dissolved in a relatively large volume of ether.

Lithium n-butoxide did not cleave benzyl chloride under the conditions of the analysis. When these two reagents were refluxed for one minute and then hydrolyzed, no chloride ion was found in the aqueous layer.

Reaction of Benzyl Chloride with n-Butyllithium. To a large excess of benzyl chloride⁽²⁴⁾ (0.6 mol) in ether was added 250 milliliters (0.158 mol) of n-butyllithium. Vigorous refluxing took place, even with a moderate rate of addition. The products isolated were: a small quantity of n-octane, five grams (21 per cent) n-nyl benzene, and 8.2 grams (31 per cent) bibenzyl. The bibenzyl was identified both by a mixed melting point determination, and the 1,3,5 trinitrobenzene - bibenzyl complex (melting point 103 to 104 °C)⁽⁶⁴⁾. Incidentally, no bibenzyl was isolated from reactions of benzyl chloride with either α -naphthyllithium or p-dimethylaminophenyl-lithium.

Capture of Benzyllithium from Reaction of Benzyl Chloride with Ethyllithium. Ethyllithium was prepared in the customary manner from 43.2 grams (0.4 mol) of ethyl bromide and 5.6 grams lithium in 400

milliliters of ether. The solution free of lithium was cooled to -50°C , and 15 grams of benzyl chloride in 50 milliliters cold ether were added rapidly⁽³⁴⁾. Under ordinary conditions, the alkyllithium compounds couple so readily with benzyl chloride that a negative color test is obtained within one-half minute after mixing the two solutions. The usual characteristic yellow color formed and the colored solution was carbonated with dry ice within one minute after the benzyl chloride was added. Subsequent to hydrolysis and removal of the ether, the solution was extracted with petroleum ether, before and after solidification. The petroleum ether and then the propionic acid were removed leaving a small quantity of oil, about 20 milligrams, having a pronounced odor of phenylacetic acid. The oil solidified after standing a week, and the phenylacetic acid was identified by the preparation of the p-bromophenacyl ester.

Reaction of Organolithium Compounds with Amines. A typical example of the reaction between an organolithium compound and an amine is described in this section.

Gaseous dimethyl amine was passed⁽²³⁾ under a pressure of 40 millimeters of mercury, through a solution of 0.15 mol of methyl-lithium in 100 milliliters of ether at room temperature for about one hour. A heavy white precipitate formed immediately and after 45 minutes an additional 50 milliliters of dry ether was added to facilitate stirring. After about one hour the solution gave a negative color test I⁽³¹⁾ the gas flow was stopped, the mixture was refluxed for 15 minutes to remove excess amine, and a color test IV⁽³⁴⁾ made at this stage was positive.

Also lithium dimethyl amide was prepared⁽²⁹⁾ by passing dimethyl amine through an ether solution containing 0.03 mol of n-butyllithium⁽²¹⁾ against a pressure of 2 to 3 centimeters of mercury⁽²³⁾. Color test IIA⁽³²⁾ was negative at the end of the reaction and color test IV⁽³⁴⁾ was positive.

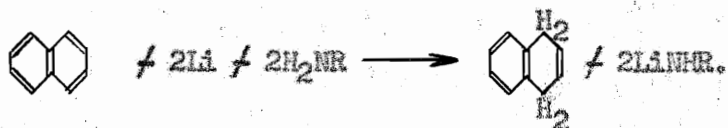
Preparation of Disubstituted Alkali-metal Amides from
Alkali-metals, Amines, and Organic Intermediates

The method invented Ziegler^(74,75,76,77) relates to a manner of producing alkali-metal substitution products of primary or secondary amines. They previously had been obtained by the action of alkali-metals^(1,2,13,69), alkali amides^(3,15), or alkali hydrides⁽³⁾ upon amines without the use of intermediates. These processes, however, have the disadvantage that they can be applied, almost exclusively, only to those amines which contain at least one aromatic or heterocyclic aromatic nucleus in the molecule. In these cases, the reaction has to be carried out at high temperatures thus unfavorably influencing the quality of the final product.

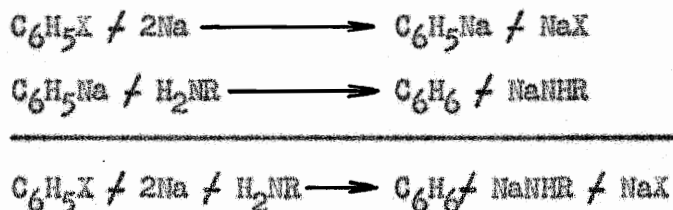
Primary and secondary purely aliphatic or alicyclic amines react with the above mentioned agents only with difficulty if at all. The alkali-metal substitution products of these amines, however, are obtained, for example, by the action of alkali organic compounds. Thus, the reaction of diethylamine with lithium phenyl or lithium butyl has already become known. The reaction described in the preceding section is similar to these two. This method, however,

has the disadvantage, that working with alkali-metal organic compounds on a large scale is inconvenient and dangerous on account of their sensitivity to shock and decomposition and their spontaneous inflammability.

Now it has been found, that the production of alkali-metal organic compounds and their action upon amines can be carried out in one operation. In this manner, the troublesome isolation of the alkali-metal organic compound is avoided and large scale preparation is made less hazardous. For example, by the action of lithium metal upon a mixture of an amine and a hydrocarbon, capable of forming alkali-metal compounds, in a suitable solvent, solutions or suspensions of lithium amides can be produced more easily. Thereby an intermediate product, which is the addition product of lithium metal to the hydrocarbon, is formed which in the nascent state reacts with the amine. The reaction is believed to take place according to the following equation when using naphthalene as the hydrocarbon capable of forming a lithium addition compound:



Instead of using hydrocarbons, halogenated alkyl or aryl hydrocarbons may be reacted with alkali-metals in the presence of amines, where the amine reacts with the alkali organic compound immediately upon formation in accordance with the following equations:



The described method enables one to use alkali organic compounds which can only be isolated with difficulty or not at all.

Butadiene or styrene may be used to advantage, since they form dihydrogenated products having low boiling points which do not interfere with the reaction. These unsaturated hydrocarbons polymerize very rapidly and readily when one uses them according to the previously known methods.

A further important advantage of the Ziegler method consists in the fact that it is often possible to produce solutions of the substituted alkali-metal amides of concentrations which cannot be prepared by simply dissolving the solid isolated metal amide in the same solvent.

Various changes and variations may be made in the reaction conditions and components without departing from the principle of the method described in this section.

Preparation of Lithium Diethyl Amide. This preparation⁽⁷⁷⁾ is an example of the method described above. To a standard three-necked flask were added 128 grams naphthalene, 14 grams of small pieces of lithium, and 150 grams of diethyl amine in a nitrogen atmosphere. The volume of the mixture was increased to one liter with absolute ether. After a few minutes, a vigorous reaction

caused the ether to boil. The reaction was stirred slowly until the end. The metal dissolved completely and an almost clear and colorless solution of the lithium diethyl amide was obtained, having a two-fold normality with respect to the dissolved lithium.

Preparation of Lithium Ethyl Anilide. This particular example⁽⁵⁾ is significant since butadiene, a gaseous unsaturated hydrocarbon having conjugated double bonds, was used. To a flask were added 104 grams of styrene or 54 grams of butadiene, in the same manner as described above, with 14 grams of lithium metal and 250 grams of ethylaniline. A two normal solution of the lithium ethyl anilide was obtained.

Preparation of Sodium Cyclohexylamide. This example⁽⁷⁷⁾ is significant since benzene was used as the solvent instead of absolute ether. To 112 grams of chlorobenzene or 92 grams of butylchloride in 500 milliliters of benzene were added, in a nitrogen atmosphere, 100 grams of dry cyclohexylamine. Into this mixture 46 grams of sodium wire were pressed. On vigorous stirring the metal was slowly transformed into a mixture of sodium cyclohexylamide and sodium chloride, the latter being suspended in the benzene.

Preparation of Disodium Dianilido Diphenylethane. This example⁽⁷⁷⁾ is significant since finely divided sodium metal was used. A suspension was made by adding 72 grams of 1,2 dianilido 1,2 diphenylethane to 1000 milliliters of absolute ether. To this suspension 16 grams of 1,3 cyclohexadiene and 10 grams of finely divided sodium metal were added while stirring, with the exclusion of any air. The sodium

metal and the suspended dianilido diphenylethane were gradually dissolved, and a yellow solution of disodium dianilido diphenylethane was formed.

Handling, Storage, and Dosage of Alkali-metal Amides

Alkali-metal amides are explosive, incendiary compounds which require particular care in handling and storage. This care is important not only to prevent danger to the user but also to preserve the purity of the alkali-metal amide.

After alkali-metal amides were prepared, they were separated from the reaction mixture, dried, and stored in lump form in an inert atmosphere. In order to protect the alkali-metal amides from atmospheric oxygen and moisture, all handling and grinding was done immediately before use. The disadvantage of this procedure was that each individual user must grind the alkali-metal amide even though in most cases suitable apparatus would not be available. Even though there is great advantage in the use of alkali-metal amides in various processes, use of the alkali-metal amides was very limited due to the disadvantage mentioned above.

Karl Ziegler⁽⁷³⁾ devised a method for transforming the alkali-metal amides so that they may be safely handled and easily dosed. This was accomplished by grinding one part of alkali-metal amide with two to six parts of an inert organic liquid in a ball mill until the alkali-metal amide was finely and evenly distributed in the organic liquid to form a paste. The consistency of this paste ranged

from that of jelly to that of butter, depending entirely on the amount of organic liquid included in the mixture. In contrast to the previous method of dry grinding, the new method was completely safe and did not require any particular precautions. The alkali-metal amide paste prepared by the new method could be safely stored, handled, and transported. The advantage of this method was that now the user could obtain the alkali-metal amide paste in which the alkali-metal amide is in a finely divided state ready for immediate use, removing any need for extra tedious preparations. The paste was sufficiently uniform, if prepared properly, that the alkali-metal amide content could be measured exactly.

In most cases the paste could be used directly without concern for undesirable effects caused by the organic liquid constituent. It was therefore desirable to let the use of the paste determine which organic liquid was to be used in preparation of the paste. Otherwise, the organic liquid, if not suitable, could be separated from the alkali-metal amide by evaporation.

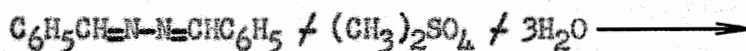
The ratio between the alkali-metal amide and the organic liquid could be varied within the limits mentioned previously. If a greater amount of liquid than recommended was used, which depended upon the particle size, undesirable sedimentation might occur. The use of too much liquid was not only a waste of the liquid, but it could cause transportation difficulties.

For many organic syntheses and reactions, alkali-metal amides in paste form gave a greater yield than as a dry powder.

Alkyl Substituted Hydrazines

Many of the alkyl substituted hydrazines have been prepared⁽⁷⁰⁾. In the methyl series, with which this investigation is concerned, all the substituted hydrazines, except tetramethylhydrazine, have been prepared, the properties of which are listed in Table VI on page 37.

Preparation of Methylhydrazine. Methylhydrazine was prepared as the sulfate⁽⁵⁰⁾, as is shown in the following equations.



In a five-liter round-bottom flask, provided with a stout glass mechanical stirrer, were placed 240 grams (1.85 mols) of powdered hydrazine sulfate, 1.8 liters of water, and 230 milliliters (207 gram, 3.4 mols) of 28 per cent aqueous ammonia (specific gravity 0.90). The mixture was stirred, and, when the hydrazine sulfate had dissolved, 440 milliliters (460 gram, 4.35 mols) of benzaldehyde were added from a separatory funnel during the course of four to five hours. After the mixture had been stirred an additional two hours, the precipitated benzalazine was filtered with suction, washed with water, and pressed thoroughly on a Blichner funnel. The product was dissolved in 800 milliliters of boiling 95 per cent ethyl alcohol, and, on cooling, the azine separated in yellow needles at 92 to 93 °C. The yield

TABLE VI

Physical Properties of Methyl Substituted Hydrazines

| Hydrazine | M. W. | Sp. Gr. | M. P. | B. P. | Solubility | | | |
|-------------------|-------|---------------------|---------------------|---------------------|------------|-----------|--------------|--------------|
| | | | | | cold water | hot water | alcohol | ether |
| Hydrazine (1) | 32.05 | 1.011 ¹⁵ | 1.4 | 113.5 | v. s. | | s. | |
| Methyl (2) | 46.07 | | -52.4 | 87.5 | v. s. | v. s. | α (3) | α (3) |
| sym.-Dimethyl (4) | 60.06 | 0.8274 | -9.0 ⁽⁵⁾ | 81.0 | v. s. | v. s. | α | α |
| unsym.-Dimethyl | 60.06 | | | 63.5 ⁽⁶⁾ | | | | |
| Trimethyl (7) | 74.08 | 0.814 | | 59.0 | | | | |
| Tetramethyl | 88.10 | | | | | | | |

- (1) Scott, J. D.: Physical Constants of Inorganic Compounds, "Handbook of Chemistry and Physics" (C. D. Hodgman, Editor in Chief), p. 522. Chemical Rubber Publishing Co., Cleveland, O., 1953. 35 ed.
- (2) Patterson, A. M.: Physical Constants of Organic Compounds, "Handbook of Chemistry and Physics" (C. D. Hodgman, Editor in Chief), p. 966. Chemical Rubber Publishing Co., Cleveland, O., 1953. 35 ed.
- (3) Bruning, G.: Ueber das Methylhydrazin, Ann., 253, 7 (1884).
- (4) Knorr, L. and A. Köhler: Ueber das symmetrische Dimethyl-hydrazin, Ber., 39, 3257 (1906).
- (5) Aston, J. G., G. J. Janz and K. E. Russel: The Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressures and Entropy of sym.-Dimethylhydrazine, J. Am. Chem. Soc., 73, 1939 (1951).
- (6) Hatt, H. H.: unsym.-Dimethylhydrazine Hydrochloride, "Organic Syntheses" (A. H. Blatt, Editor), Vol. II, p. 206. John Wiley and Sons, Inc., New York, N. Y. 1943. revised ed.
- (7) Class, J. B. and J. G. Aston: Synthesis and Properties of Trimethylhydrazine, J. Am. Chem. Soc., 73, 2359 (1951).

was 350 - 360 grams (91-94 per cent of the theoretical amount).

Theazine was freed of ethyl alcohol by drying in a vacuum desiccator over calcium chloride.

Two hundred grams (0.96 mol) of benzalazine, 350 milliliters of dry, thiophene-free benzene, and 100 milliliters (133 grams, 1.05 moles) of methyl sulfate were mixed in a three-liter round-bottomed flask, provided with a reflux condenser bearing a calcium chloride tube. The mixture was heated continuously, with occasional shaking, on a water bath and gently refluxed for five hours. The mixture was cooled, and the solid addition product was decomposed by adding 600 milliliters of water and shaking until all the solid material had disappeared. The benzene and benzaldehyde were removed by steam distillation. The residual liquor, after cooling, was treated with 15 - 20 milliliters of benzaldehyde and left overnight. The resin and benzalazine were separated by filtration.

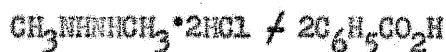
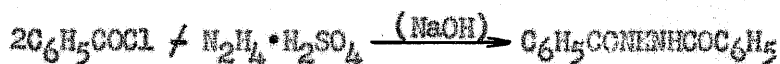
The filtrate was evaporated under reduced pressure on a water bath until a semi-crystalline mass remained. This was further desiccated by evaporating twice under reduced pressure with 50-milliliter portions of absolute ethyl alcohol. The resulting crystalline cake was crushed with 50 milliliters of absolute ethyl alcohol, filtered, and the process repeated. The white, crystalline product was almost pure methylhydrazine sulfate and contained very little hydrazine sulfate. After drying in a vacuum desiccator over calcium chloride, the yield was 105 - 110 grams (76-80 per cent of the theoretical amount). For purification, the sulfate was dissolved

in 250 milliliters of boiling 80 per cent ethyl alcohol, and any undissolved material was filtered out. On cooling, the methylhydrazine sulfate separated as white plates, which were filtered with suction and washed with a little absolute alcohol. After drying over calcium chloride, the first fraction, melting point 141 - 142 °C, weighed 70 - 75 grams (51-54 per cent of the theoretical amount).

This procedure was essentially the method of Thiele⁽⁶⁷⁾. Methylhydrazine has been prepared also by reduction and subsequent hydrolysis of nitrosomethylurea⁽⁹⁾, nitromethylurethane⁽⁶⁾, and nitrosomethylamine sulfonic acid⁽⁶⁸⁾, and by methylation of hydrazine hydrate with methyl iodide⁽⁴⁶⁾ or diazomethane⁽⁶³⁾.

Preparation of sym.-Dimethylhydrazine Dihydrochloride.

sym-Dimethylhydrazine was prepared as the dihydrochloride⁽⁴⁸⁾, as is shown in the following equations.



In a two-liter flask, provided with a mechanical stirrer and cooled in a bath of cold water, were placed a solution of 48 grams

(1.2 mols) of sodium hydroxide in 500 milliliters of water and 65 grams (0.5 mol) of hydrazine sulfate. With stirring, 145 grams (120 milliliters, 1.03 mols) of freshly distilled benzoyl chloride and 120 milliliters of an aqueous solution containing 45 grams (1.1 mols) of sodium hydroxide were added slowly from separate dropping funnels. The benzoyl chloride was added over a period of 1.5 hours. The alkali was added slightly faster. After both additions were completed the mixture was stirred for two hours longer and then saturated with carbon dioxide. The dibenzoylhydrazine was filtered with suction, pressed thoroughly, and ground to a paste with 50 per cent aqueous acetone. The material was filtered with suction, washed with water, and pressed as dry as possible. The crude product was dissolved in about 650 milliliters of boiling glacial acetic acid, from which, on cooling, the dibenzoylhydrazine separated as a mass of fine white needles. These were filtered with suction, washed with cold water, and dried by heating under reduced pressure on a water bath, in a slow current of air. This first fraction, melting point $234 - 238^{\circ}\text{C}$, amounted to 80 - 90 grams (66-75 per cent of the theoretical amount) and was practically pure.

The following operations should be performed under a hood. In a two-liter three-necked flask, provided with a mechanical stirrer, a thermometer, and two dropping funnels, were placed 80 grams (0.33 mol) of dibenzoylhydrazine, 10 grams (0.25 mol) of sodium hydroxide, and 600 milliliters of water. The mixture was maintained at about 90°C by heating on a water bath. With stirring,

320 grams (240 milliliters, 2.54 mols) of methyl sulfate and 250 milliliters of an aqueous solution containing 125 grams (3.1 mols) of sodium hydroxide were added from separate dropping funnels. The methyl sulfate was added in 10-milliliter portions at five-minute intervals, the sodium hydroxide solution at such a rate that the reaction mixture was maintained slightly alkaline. When markedly alkaline, the mixture had a distinctive yellow color; it was best to maintain a degree of alkalinity slightly less than that required to produce this color.

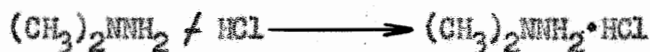
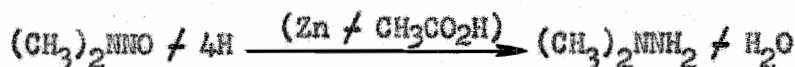
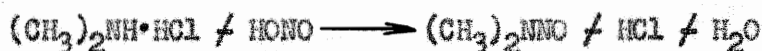
During the additions, which required about two hours, the dibenzoyldimethylhydrazine separated as a supernatant liquid. The semisolid material thrown up on the sides of the flask was washed down from time to time. After being heated for one-half hour longer the mixture was allowed to cool. The solid dibenzoyldimethylhydrazine was collected, crushed with water, filtered, and dissolved in 100 milliliters of chloroform. The solution was filtered from insoluble impurities and dried over sodium sulfate. The chloroform was removed by heating on a water bath, and finally under reduced pressure. The solid residue melted at $77 - 84^{\circ}\text{C}$ and was sufficiently pure for further use. The yield was 77 - 83 grams (86-93 per cent of the theoretical amount).

In a two-liter flask, a mixture of 67 grams (0.25 mol) of dibenzoyldimethylhydrazine and 250 milliliters of 32 per cent hydrochloric acid (specific gravity 1.16) was refluxed gently for two hours under a hood. To remove the benzoic acid, the mixture was steam

distilled until 10 liters of distillate had collected. The residual liquor was evaporated to dryness under reduced pressure on a water bath. The crystalline dihydrochloride was treated with 25 milliliters of absolute ethyl alcohol, and the mixture was evaporated to dryness under reduced pressure. This treatment was repeated, and the dihydrochloride was crushed with a mixture of 25 milliliters absolute alcohol and 2 - 3 milliliters of concentrated hydrochloric acid, filtered, and washed with 10 - 15 milliliters of cold absolute alcohol. The first fraction of dimethylhydrazine dihydrochloride, after being dried in a vacuum desiccator, weighed 22 - 23 grams.

Symmetrical dimethylhydrazine has been obtained by heating the methiodide of 1-methylpyrazole with potassium hydroxide⁽⁵²⁾. It has usually been prepared by methylation of diformylhydrazine and subsequent hydrolysis with hydrochloric acid^(46,47,66). The method described was based on the observation of Folpmers that dibenzoylhydrazine might be similarly employed⁽¹⁷⁾.

Preparation of unsym.-Dimethylhydrazine Hydrochloride. In this preparation unsym-dimethylhydrazine was prepared as the hydrochloride⁽⁴⁹⁾ as shown in the following equations.



In a two-liter round-bottomed flask provided with a mechanical stirrer were placed 245 grams (3 mols) of dimethylamine hydrochloride,

120 milliliters of water, and 10 milliliters of approximately two normal hydrochloric acid. The resulting solution was stirred vigorously and maintained at 70 - 75 °C by heating on a water bath, while 235 grams (3.23 mols) of 95 per cent sodium nitrite suspended in 150 milliliters of water were added from a dropping funnel over a period of an hour. The reaction mixture was tested frequently and maintained barely acid to litmus by further one milliliter additions of two normal hydrochloric acid when necessary. Stirring and heating were continued for two hours after all the sodium nitrite had been added.

The flask was arranged for distillation, and the reaction mixture was distilled under slightly reduced pressure on a water bath until the residue was practically dry. To the residue 100 milliliters of water were added, and the process of distillation to dryness was repeated. The distillates were combined and saturated with potassium carbonate. The upper layer of dimethylnitrosoamine was removed, and the water layer was extracted with three 140-milliliter portions of ether. The combined nitrosoamine and ethereal extracts were dried over anhydrous potassium carbonate and distilled through a 30-centimeter fractionating column. The yield of product boiling at 149 - 150 °C at 755 millimeters of mercury was 195 - 200 grams (88-90 per cent of the theoretical amount). Nitrosodimethylamine is a yellow oil which darkens in bright light.

In a five-liter round-bottomed flask, provided with a mechanical stirrer, dropping funnel, and thermometer, 200 grams (2.7 mols) of

nitrosodimethylamine, three liters of water, and 650 grams (10 gram atoms) of 100 per cent zinc dust, or an equivalent amount of lower quality material were mixed. While the mixture was stirred and maintained at 25 - 30 °C by immersion in a water bath, one liter (14 mols) of 85 per cent acetic acid was added from the dropping funnel over a period of two hours. Subsequently the reaction mixture was heated for one hour at 60 °C, allowed to cool, and the excess zinc dust filtered and washed with a little water. The aqueous liquors were combined and transferred to a 12 liter flask arranged for steam distillation. The flask was fitted with a dropping funnel, and the steam inlet was provided with a trap. A large filtering or distilling flask served as a receiver, and the side tube was connected with two absorption flasks, each containing 1:1 hydrochloric acid. The aqueous liquors were made distinctly alkaline by adding a concentrated solution of 1000 grams of sodium hydroxide through the dropping funnel, and the mixture was then steam distilled until a test portion of the distillate showed only a faint reduction with Fehling's solution.

The aqueous distillate was treated with 650 milliliters of concentrated hydrochloric acid and concentrated on a steam bath, under reduced pressure, until the residual liquor became a syrupy mass. This was desiccated further by adding 150 milliliters of absolute ethyl alcohol and evaporating under reduced pressure. Two or three such treatments with alcohol dried the crystalline material sufficiently so that it no longer stuck to the sides of the flask. The

crude product was dried further in a vacuum desiccator over calcium chloride. The pale yellow, dry, crystalline solid weighed 200 - 215 grams (77-83 per cent of the theoretical amount). The dried product could be purified by dissolving it in an equal weight of boiling absolute ethyl alcohol and then chilling in an ice bath. The yield of pure white crystals melting at 81 - 82 °C was 180 - 190 grams (69-73 per cent of the theoretical amount).

The preparation of unsymmetrical dimethylhydrazine by reduction of nitrosodimethylamine was also described by Fischer⁽¹⁶⁾ and by Renouf⁽⁵⁷⁾. Methylation of hydrazine⁽⁴⁶⁾, reduction of nitrodimethylamine^(5,18), and the action of aminopersulfuric acid on dimethylamine⁽⁶⁰⁾ also furnish unsymmetrical dimethylhydrazine.

Preparation of Trimethylhydrazine. Attempts by Klages and coworkers⁽⁵¹⁾ indicated the impracticability of chloramine coupling and methylation, so Class and Aston⁽¹²⁾ attempted and succeeded in reducing N,N-dimethyl N'-methylene hydrazine with lithium aluminum hydride.

Identification of the product resulted from equivalent weight determinations by electrometric titration with hydrochloric acid. The equivalent weight calculated was 74.13, found 74.53 and 74.59. A cryoscopic determination in water gave a molecular weight of 67.2, calculated 74.13, indicating one equivalent per molecule.

Trimethylhydrazine is a colorless liquid possessing a strong, fishlike odor. Unlike hydrazine and the other known methylhydrazines it is relatively stable to the atmosphere. The compound fumes on

dilution with water, the process of dilution being strongly exothermic. The low boiling point of 59 °C, which is lower than that of the methyl and dimethylhydrazines, indicates that the hydrogen bonding characteristics of hydrazine is further decreased by introducing a third methyl group.

III. EXPERIMENTAL

The experimental section includes the purpose of the investigation, the plan of experimentation, and all information relating to actual laboratory material, apparatus, procedures, data obtained, and results calculated.

Purpose of Investigation

The purpose of this investigation is to determine the products of the electrolysis of lithium dimethyl amide in non-aqueous solvents.

Plan of Experimentation

This investigation consisted of a literature review, assembly of equipment and materials, construction of suitable apparatus, and experimental work.

Literature Review. A literature review was made through references, texts, and periodicals for published material on the preparation and properties of disubstituted alkali-metal amides, substituted hydrazines, and similar compounds.

Equipment and Materials. Necessary apparatus, such as reaction, distillation, hydrolysis, and electrolysis apparatus was constructed from laboratory glassware fitted with standard-taper joints. Chemicals, such as lithium, sodium, dimethyl, diethyl, and di-normal-butyl amines,

and an extensive variety of non-aqueous solvents were obtained from local laboratory supply houses.

Preparation of di-Substituted Alkali-metal Amides. Preparation of Di-substituted alkali-metal amides was attempted by reacting sodium with dimethyl-, diethyl-, and di-normal-butyl amine in the presence of naphthalene dissolved in diethyl ether or in the presence of 1,3 butadiene; lithium with dimethyl and diethyl amine in the presence of naphthalene dissolved in diethyl ether or in the presence of 1,3 butadiene; and butyllithium with dimethyl amine in the presence of diethyl or petroleum ether.

The preparations were carried out on a half mole basis. Preparation of di-normal-butyl sodamide was attempted first, because sodium is easier to handle than lithium and with di-normal-butyl amine a larger yield may be expected. This simplified the analytical work. After study of this preparation and other preparations with diethyl amine, gaseous dimethyl amine was used in subsequent reactions with sodium and then lithium.

Determination of Properties. After the product was separated from the reaction mixture, its behavior in air, water, under impact, and at elevated temperature was determined. A melting point determination was made in a glycerine bath. The product was then analyzed for amine and alkali content. Further analysis as to carbon, hydrogen, and nitrogen content was made by a commercial analytical laboratory.

Electrolysis. Fusion of dimethyl lithium amide was attempted. Then solubility determinations were made. Electrolyses in a mercury-

platinum electrolytic cell in solvents showing solubility were attempted.

Analysis of Products of Electrolysis. The product was separated from the reaction mixture and the mercury by decanting and from the liquid ammonia by distillation. The behavior of the product in air, water, and under impact was determined. The molecular weight of the product was determined by titration and the lowering of the freezing point of benzene. An elemental analysis for carbon, hydrogen, and nitrogen content was made by a commercial analytical laboratory.

Materials

The following materials were used in this investigation.

Acetone. Reagent grade, code No 1004, lot No K152.

Specifications: "Meets A.C.S. standards." Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N.Y.

Used with dry ice as condensing bath.

Alcohol, Methyl. Absolute, code No 1214, lot No J331J.

Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N.Y. Used with dry ice as condensing agent for dimethyl amine and butadiene 1,3, and as solvent.

Ammonia. Obtained from Armour Ammonia Division, North Bergen, N.J. Used as test solvent.

Benzene. Purified, 99 - 100 %, code No 1444, lot No H086.

Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N.Y. Used as test solvent.

1-Bromobutane. Code No 51. Obtained from Eastman Kodak Co., Rochester, N.Y. Used in preparation of butyllithium.

Butadiene 1,3. CP. Obtained from The Matheson Co., Inc., East Rutherford, N.J. Used as catalyst for preparation of dimethyl sodium amide.

Calcium Chloride. Anhydrous, No 20 mesh, code No 1502, lot No H020. Specifications: "Assay minimum, 96.0 %; maximum limit of impurities, alkalinity (as calcium hydroxide), 0.020 %; Mg and alkali salts (as sulfates), 2.0 %." Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N.Y. Used in drying tubes.

Carbon Tetrachloride. Code No 1554, lot No G025J. Meets A.C.S. specifications; boiling range, 76 - 78 °C. Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N.Y. Used as test solvent.

1-Chlorobutane. Code No 52. Obtained from Eastman Kodak Co., Rochester, N.Y. Used in preparation of butyllithium.

Chloroform. USP, code No C-296, control No G2201. Obtained from Fisher Scientific Co., Silver Spring, Md. Used as test solvent.

Chromel Wire. Chromel-P, gage 18, coil No 6773 C. Manufactured by Hoskins Mfg. Co., Detroit 8, Mich. Used to connect mercury cathode with current source in electrolysis.

Copper Wire. Annunciator wire, No 18. Obtained from Blacksburg Hardware Co., Blacksburg, Va. Used as conductor in electrolysis.

Diethyl Amine. CP, code No D-46. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to prepare diethyl sodium and lithium amide.

Dimethyl Amine. Anhydrous. Obtained from The Matheson Co., Inc., East Rutherford, N.J. Used to prepare dimethyl sodium and lithium amide.

Di-n-butyl Amine. Code No 1260. Obtained from Eastman Kodak Co., Rochester, N.Y. Used to prepare di-n-butyl sodium amide.

Drierite. Anhydrous calcium sulfate, size 6 mesh. Manufactured by W. A. Hammond Drierite Co., Xenia, Ohio. Used in drying tubes.

Ether, Ethyl. Code No 1699, lot No J355J. Dry, code No 1706, lot No J083J. Specifications: "Meets A.C.S. standards, specific gravity 25°/25°C, 0.712 - 0.714. Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N.Y. Used as solvent.

Glass Wool. Obtained from Fisher Scientific Co., Silver Spring, Md. Used as filtration agent for organolithium compounds.

Glycerine. USP, white, code No G-32, control No 90211. Obtained from Fisher Scientific Co., Silver Spring, Md. Used as bath in melting point determination.

Hydrochloric Acid. CP, catalog No A-144. Specifications: "Specific gravity, 1.1878 at 60 °F; purity, not less than 37 % hydrochloric acid by volume." Obtained from Fisher Scientific Co., Silver Spring, Md. Used in analysis for amine content.

Ice, Dry. Solid carbon dioxide. Obtained from Clover Creamery, Radford, Va. Used with methyl alcohol and acetone to condense dimethyl amine and butadiene 1,3.

Lithium Metal. CP, code No L-111, control No 510420. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to prepare disubstituted lithium amides.

Lithium Metal. Wire, one-eighth inch diameter. Obtained from A.D. McKay Inc., New York 38, N.Y. Used to prepare butyllithium.

Mercury. Technical. Manufactured by Metal Salts Corp., Hawthorne, N.J. Used as an atmospheric seal and cathode.

Mineral Oil. USP, heavy, white. Obtained from Tech Drug Store, Blacksburg, Va. Used as a storing medium for lithium and sodium metal.

Naphthalene. Reagent grade, code No 2001, lot No HL33. Specifications: "Maximum limits of impurities, nonvolatile 0.002 %." Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N.Y. Used as an intermediate in the preparation of some disubstituted alkali metal amides and naphthyllithium.

Nitrogen. Oil pumped. Obtained from The Matheson Co., Inc., East Rutherford, N.J. Obtained from Southern Oxygen Co., Roanoke, Va. Used as inert atmosphere.

Oxalic Acid. Crystalline. Lot No 51846. Obtained from J. T. Baker Chemical Co., Phillipsburg, N.J. Used as standard for sodium hydroxide solutions.

Petroleum Ether. CP, catalog No E-139. Analysis: "Appearance and color, clear and colorless; odor, passes test; boiling range, 32 - 57.2 °C; free acid, none; fats and oils, none; nonvolatile matter, 0.001 %." Obtained from Fisher Scientific Co., Silver Spring, Md. Used as solvent.

Phenolphthalein. Powder, USP, code No 2051, lot No 23. Obtained from General Chemical Co., New York, N.Y. Used as indicator.

Platinum. Sheet. Obtained from Chemical Engineering Department, Virginia Polytechnic Institute, Blacksburg, Va. Used as anode in electrolysis of dimethyl lithium amide.

Sodium Carbonate. Anhydrous powder, code No 2248, lot No H002. Meets A.C.S. specifications. Obtained from General Chemical Division, Allied Chemical and Dye Corp., New York, N.Y. Used as standard for hydrochloric acid solutions.

Sodium Hydride. Lot No 921. Obtained from Metal Hydrides Inc., Beverly, Mass. Used to dry ether.

Sodium Hydroxide. Pellets, code No 7708, control No WXSX. Specifications: "Meets with A.C.S. standards." Obtained from Mallinckrodt Chemical Works, New York, N.Y. Used for analysis.

Sodium Metal. Analytical reagent, code No 7348, control No KMX. Manufactured by Mallinckrodt Chemical Works, New York, N.Y. Obtained from Fisher Scientific Co., Silver Spring, Md. Used in the preparation of disubstituted sodium amides.

Sulfuric Acid. CP, code No 1180. Specifications: "Assay, 95.5 - 96.5 %; specific gravity, 1.84. Obtained from General Chemical

Division, Allied Chemical and Dye Corp., New York, N.Y. Used in analysis for lithium and sodium.

Toluene. GP, catalog No T-324. Specifications: "Boiling range, 110 - 111 °C; nonvolatile matter, 0.001 %; substances darkened by sulfuric acid, none; sulfur compounds, 0.000 %; water, 0.02 %." Obtained from Fisher Scientific Co., Silver Spring, Md. Used as solvent and to prepare sodium dispersion.

Water, Distilled. Once distilled from well water from Virginia Polytechnic Institute, Blacksburg, Va. Used as solvent and diluent.

Apparatus

The apparatus enumerated below was used in this investigation.

Ammeter. Direct Current, ranges: 0 - 3 amperes in 0.05-ampere divisions, 0 - 30 amperes in 0.5-ampere divisions, model 489, serial No 6523. Manufactured by Weston Electrical Instrument Corp., Newark, N.J. Used to measure current used in electrolysis.

Balance, Analytical Chain. Capacity 200 grams, sensitivity 0.0001 gram. Manufactured by Seederer-Kohlbusch Inc., Jersey City, N.J. Used to weigh product samples for analysis.

Balance, Triplebeam. Capacity 610 grams, sensitivity 0.1 gram. Manufactured by Ohaus, Newark, N.J. Obtained from Phipps and Bird Inc., Richmond, Va. Used to weigh chemicals.

Generator, Direct Current. Shunt wound, serial No 726, 55 volts, 90 amperes, 1750 revolutions per minute, 5 kilowatt. Manufactured by

The Hertner Electric Co., Cleveland, O. Obtained from L. J. Land Inc., New York, N.Y. Used as the direct current source for electrolysis.

Heater, Forma. Catalog No 1012, No 94, capacity 500 milliliters, 115 volts, 400 watts. Manufactured by the Forma-Scientific Co., Marietta, O. Used to heat reaction flask.

Heater, Autemp. Alternating current, 115 volts. Obtained from Fisher Scientific Co., Silver Spring, Md. Used as an all purpose heater.

Ice Machine. Manufactured by Victor Products Corp., Hagerstown, Md. Used to supply ice for cooling reactions and freezing point determinations.

Motor. Electric, alternating current, model No S60SBZ-1820, type S, frame 562, horsepower $\frac{1}{4}$, 1725 revolutions per minute, 115 volts, 4.6 amperes, 60 cycles, ph 1, code R, temperature rise 50 °C cont., No 33A - 33, NP 2192. Manufactured by Emerson Electric Co., St. Louis, Mo. Obtained from Central Scientific Co., Chicago, Ill. Used to drive Cenco Pressovac 4 Pump.

Oscillograph, Cathode-Ray. Type 274-A, serial No 2306, 115/230 volts, 50 - 60 cycles, 50 watts. Manufactured by Allen B. Dumont Laboratories Inc., Passaic, N.J. Used to measure conductivity of product of electrolysis in nonaqueous solvents.

Oven, Electric Utility. Model OV 8, serial No 8-270, 115 volts, 5 amperes. Manufactured by Modern Electric Laboratory, Chicago, Ill.

Obtained from Scientific Glass Apparatus Co., Inc., Bloomfield, N.J.

Used to dry apparatus.

pH Meter. Glass electrode, model H2, serial No 82580. Manufactured by Beckman Instruments Inc., South Pasadena, Cal. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to determine titration curves of products.

Pipettor, Caulfield. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to transfer amides for analysis.

Powerstat. Type 116, 115 volts, 50-60 cycles, output range 0 - 135 volts, maximum one kilovolt, 7.5 amperes. Manufactured by The Superior Electric Co., Bristol, Conn. Used to regulate heaters.

Pump, Cenco Pressovac 4. Maximum speed 600 revolutions per minute, maximum pressure 10 pounds per square inch. Manufactured by Central Scientific Co., Chicago, Ill. Used to remove low boiling solvents.

Resistance, Variable. Catalog No 4261, serial No 1003353. Manufactured by Leeds and Northrup Co., Philadelphia, Pa. Used in conjunction with the oscillograph to measure conductivity.

Resistor, Decade. No 82821D, capacity 99,990 ohms. Manufactured by Central Scientific Co., Chicago, Ill. Used in conjunction with the oscillograph to measure conductivity.

Rheostat. No 8070-B1, DL 2240005, G138, maximum voltage 250 volts, 25 ohms, 5.2 amperes, resistance 3.41 ohms, for Field. Manufactured by General Electric, Schenectady, N.Y. Used to control direct current generator.

Stirrer, Magnetic. Volts 115, 50 - 60 cycles. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to stir reaction mixture.

Stirrer, Magnetic. Magna-Stir, 115 volts, 50-60 cycles. Manufactured by Laboratory Industries, Inc., Chicago, Ill. Used to stir reaction mixture.

Stirrer, Cenco Variable Speed. Catalog No 18805, 115 volts alternating current, 60 cycles, 0.68 amperes, No 1256583, type NST-12. Manufactured by Central Scientific Co., Chicago, Ill. Used to stir reaction mixture.

Switch, Safety. Catalog No DF 322, style 1292546D, 60 amperes, 230 volts alternating current. Manufactured by Westinghouse Electric Corp., Pittsburgh, Pa. Used to control direct current generator.

Thermometer. Ground glass joint, mercury filled, range -10 to 360 °C in 1 ° divisions. Obtained from Fisher Scientific Co., Silver Spring, Md. Used with ground glass distillation apparatus.

Thermometer. Catalog No 15-035, range -100 to 50 °C in 1 ° divisions. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to measure temperature of butyllithium reaction.

Thermometer. Standard laboratory, mercury filled, catalog No 14-985, range -20 to 110 °C in 1 ° divisions. Obtained from Fisher Scientific Co., Silver Spring, Md. Used to measure reaction temperatures.

Variac. Volts output 0 - 135, 5 amperes, 50 - 60 cycles. Manufactured by general Radio Co., Cambridge, Mass. Used to regulate heaters.

Voltmeter. Direct current, ranges: 0 - 3 volts in 0.05 volt divisions, 0 - 7.5 volts in 0.1 volt divisions, 0 - 150 volts in 1.0 volt divisions, model 489. Manufactured by Weston Electrical Instrument Corp., Newark, N.J. Used to measure potential in electrolysis.

Method of Procedure

This section contains descriptions of methods used to prepare reagents, construct apparatus, carry out reactions, and analyze products of the reactions.

Preparation of Alkali-metals. Sodium metal was obtained in cans containing one pound blocks in a vacuum. The top was cut from the can, and the block of sodium metal was removed. With a sharp clean knife, the block was cut into smaller pieces, measuring on the average 1 x 1 x 5 inches, on a flat, clean surface. These pieces were stored in glass bottles with plastic screw caps, under an inert oil such as mineral oil. When the sodium was needed for a reaction, a piece was removed from the storage bottle, trimmed of oxide, and divided into suitable chips with a sharp clean knife. Either the trimmed block or the chips were weighed on a triple beam balance to determine the amount of sodium. The metal was rinsed with ether before it was added to the reaction.

A suspension of high surface sodium was prepared in the following manner. A standard, three-necked flask, A, was fitted with a stopper,

an air-tight mercury-seal stirrer, B, a gas inlet adapter, C, and a mercury bubbler, D, as shown in Figure 2 on page 60. The stirrer was connected with a variable speed motor, and a nitrogen supply was connected with bubbler D.

Into flask A, 500 milliliters of freshly distilled toluene were placed, and 12 grams of sodium metal were added in one-half inch cubes, in a nitrogen atmosphere. The contents were gradually heated with a heater, E, controlled with a voltage regulator and the stirrer was set in motion. The stopper was replaced with a thermometer. When the toluene (boiling point 110.8°C)⁽⁵⁵⁾, attained a temperature of 98°C , the cubes of sodium (melting point 97.5°C)⁽⁵⁹⁾ broke up into smaller irregular particles which formed beads with an average diameter of one to two millimeters. While stirring, the heater was replaced with a cold water bath. When the contents attained room temperature, the stirrer was stopped.

At first, lithium metal was divided in the same manner as sodium, but this procedure was proved to be tedious and very time consuming. Thereafter, lithium blocks of suitable size, wet with mineral oil, were hammered into flat sheets, two millimeters thick, in a shallow copper pan. The flat sheets of lithium were cut into strips, five millimeters wide, and then the strips were cut into pieces, three millimeters wide, with sharp scissors. The small pieces were weighed, rinsed with ether and added to the reaction.

In some reactions lithium wire was used. Several lengths of the wire were measured and weighed to obtain a correlation between weight

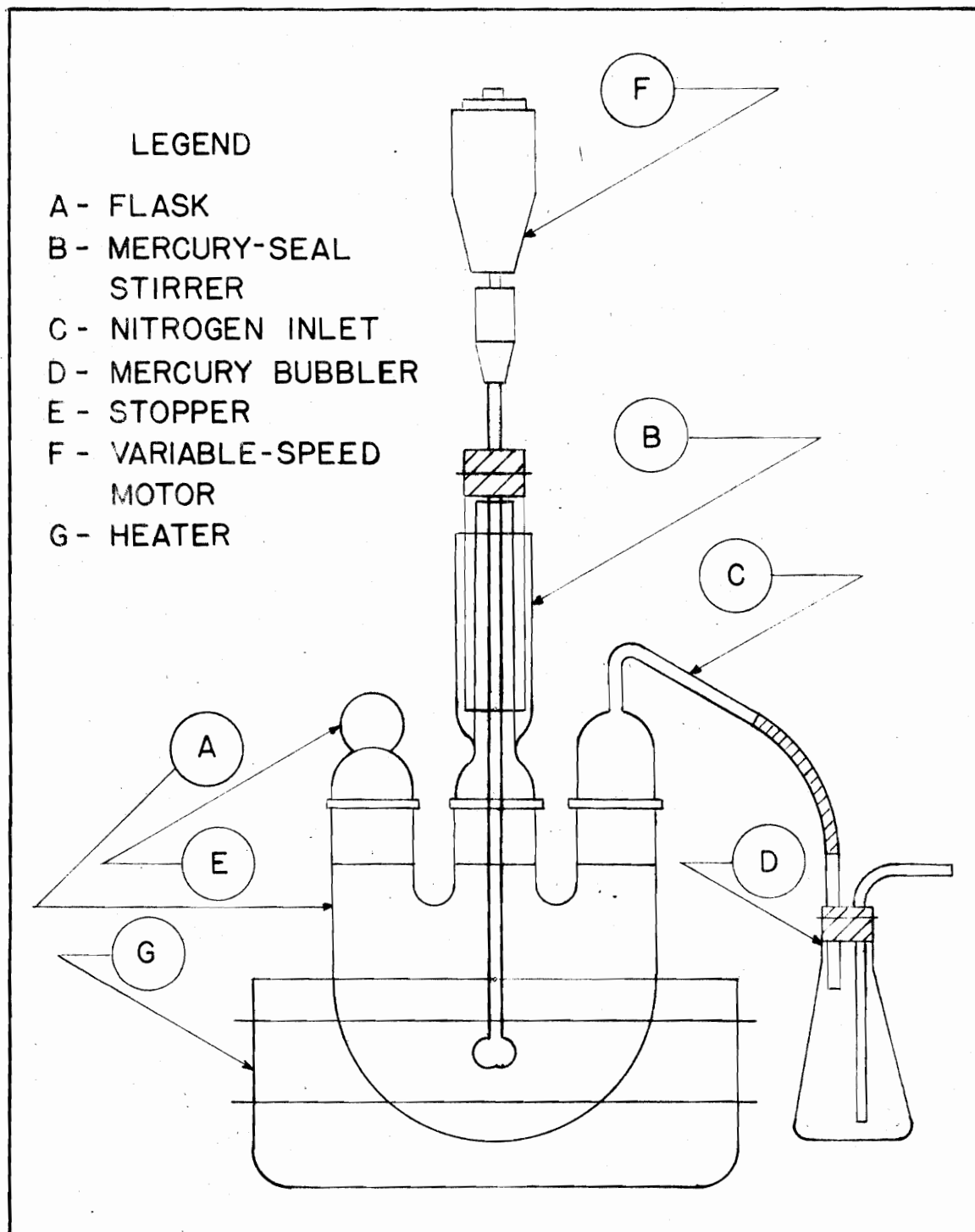


FIGURE 2. APPARATUS FOR THE PREPARATION OF HIGH SURFACE SODIUM DISPERSIONS

and length. The needed amount of lithium wire was measured, rinsed in ether and cut with scissors directly into the reaction flask.

Drying Ether. Diethyl and petroleum ether were dried as follows. Approximately one liter was placed into a four-liter erlenmeyer flask. A small amount of sodium hydride, about one to two grams, was carefully added to the ether. A large rubber stopper was laid over the mouth of the flask, and the ether was allowed to stand overnight, or until all bubbling had ceased. The ether was then decanted into a distillation setup and distilled, but not to dryness.

Cleaning and Drying Mercury. Before laboratory mercury could be used in bubblers and as a cathode, it had to be cleaned and dried. A 1000-milliliter graduate cylinder was filled with 500 milliliters of a 10 per cent nitric acid solution. A small filter funnel with filter paper was placed on top of the graduate. A very fine hole was made in the filter paper with a pin. The mercury was placed in the filter funnel and permitted to drop into the nitric acid solution as a fine spray. This procedure was repeated. The nitric acid was washed from the mercury with flowing water, until the wet mercury was neutral to litmus paper. Most of the water was removed from the mercury by decanting and blotting. The remaining water was evaporated from the mercury under vacuum.

Preparation of Di-n-butyl Sodium Amide. A standard, ground glass, three-necked, two-liter flask was fitted with a mercury-seal stirrer, a nitrogen inlet, and a vent tube connected to a water bubbler. The nitrogen inlet was connected to a nitrogen tank with rubber tubing.

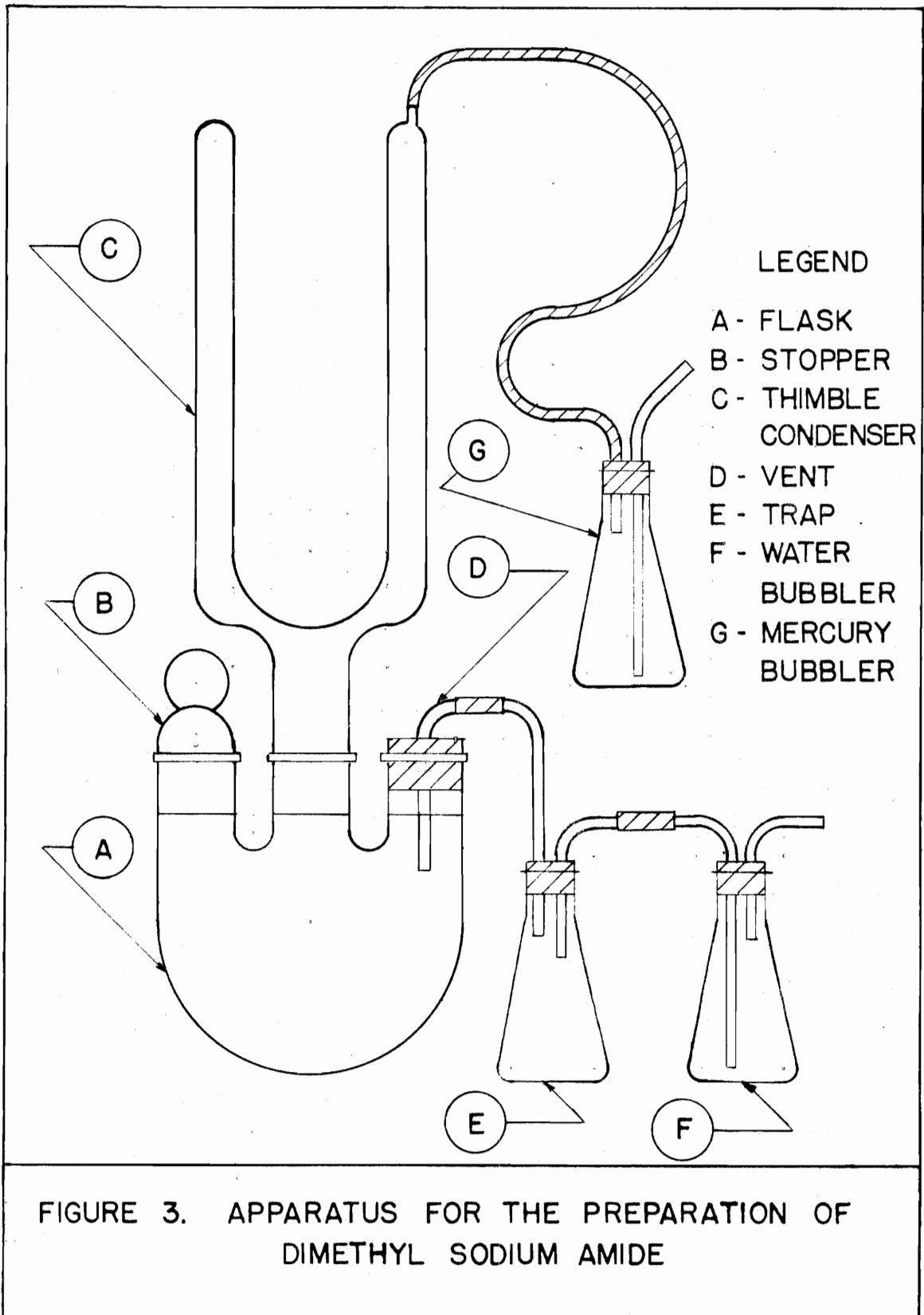
To the flask were added 32.1 grams (0.25 mol) of naphthalene, 32.5 grams (0.25 mol) of di-n-butyl amine, and 15 grams (0.5 mol plus excess of 0.15 mol) of sodium in small pieces 10 millimeters square and 20 millimeters long. The volume was made up to one liter with ether. Nitrogen was passed through the flask, and the mixture was stirred for three hours and 15 minutes.

The white precipitate, formed during the reaction and the unreacted sodium metal were separated from the reaction mixture by filtration in a Büchner funnel. The solid was dried in a stream of nitrogen and bottled under nitrogen as di-n-butyl sodium amide with some sodium metal.

Preparation of Dimethyl Sodium Amide. This preparation was attempted with three variations. Naphthalene and 1, 3 butadiene were used as the hydrocarbon alkali-metal carrier, and when 1, 3 butadiene was used, both lump and dispersed sodium was used.

The apparatus assembled for this preparation is shown in Figure 3 on page 63. A standard, ground glass, three-necked, two liter flask, A, was fitted with a ground glass stopper, B, a thimble condenser, C, and a vent tube, D, which was connected with a trap, E, and a bubbler, F. Water was used in the bubbler to absorb any escaping dimethyl amine. A mercury bubbler, G, was connected with the gas source to be used.

The apparatus was flushed with dimethyl amine to replace any air. The thimble condenser was filled with a methyl alcohol - dry ice mixture. To the flask, 1.4 grams of sodium shavings were added.



Dimethyl amine and 1,3 butadiene were condensed upon the sodium alternately for five-minute periods for one hour and 10 minutes. The white precipitate, which was formed in the reaction, was separated from the mixture with a sintered glass filter, in the absence of air, as shown in Figure 4, on page 65. The solid residue was dried in a stream of nitrogen and placed in a container.

The preparation was repeated on a molar scale. The apparatus was flushed with nitrogen, and 22.5 grams (one mol) of sodium were added in five-millimeter cubes. Butadiene, 1,3 was condensed upon the sodium for 30 minutes, dimethyl amine for one hour, 1,3 butadiene for another 30 minutes, and dimethyl amine for 15 more minutes. After addition of the gas the mixture was permitted to reflux for two hours until the dry ice in the condenser had evaporated.

A sodium dispersion in toluene was added to the flask in another preparation. The 1,3 butadiene and dimethyl amine were condensed for 30-minute periods alternately for four hours into the sodium suspension.

Naphthalene was substituted for 1,3 butadiene in one preparation. A stirring magnet was placed in the flask and a magnetic stirrer under it. To the flask were added 64 grams (0.5 mol) of naphthalene, 23 grams (one mol) sodium, in small pieces measuring 5 x 5 x 10 millimeters, and ether to make the volume one liter. The mixture was agitated with the magnetic stirrer until the naphthalene had dissolved in the ether. A mixture of dry ice and methyl alcohol was placed into the thimble condenser, and dimethyl amine was

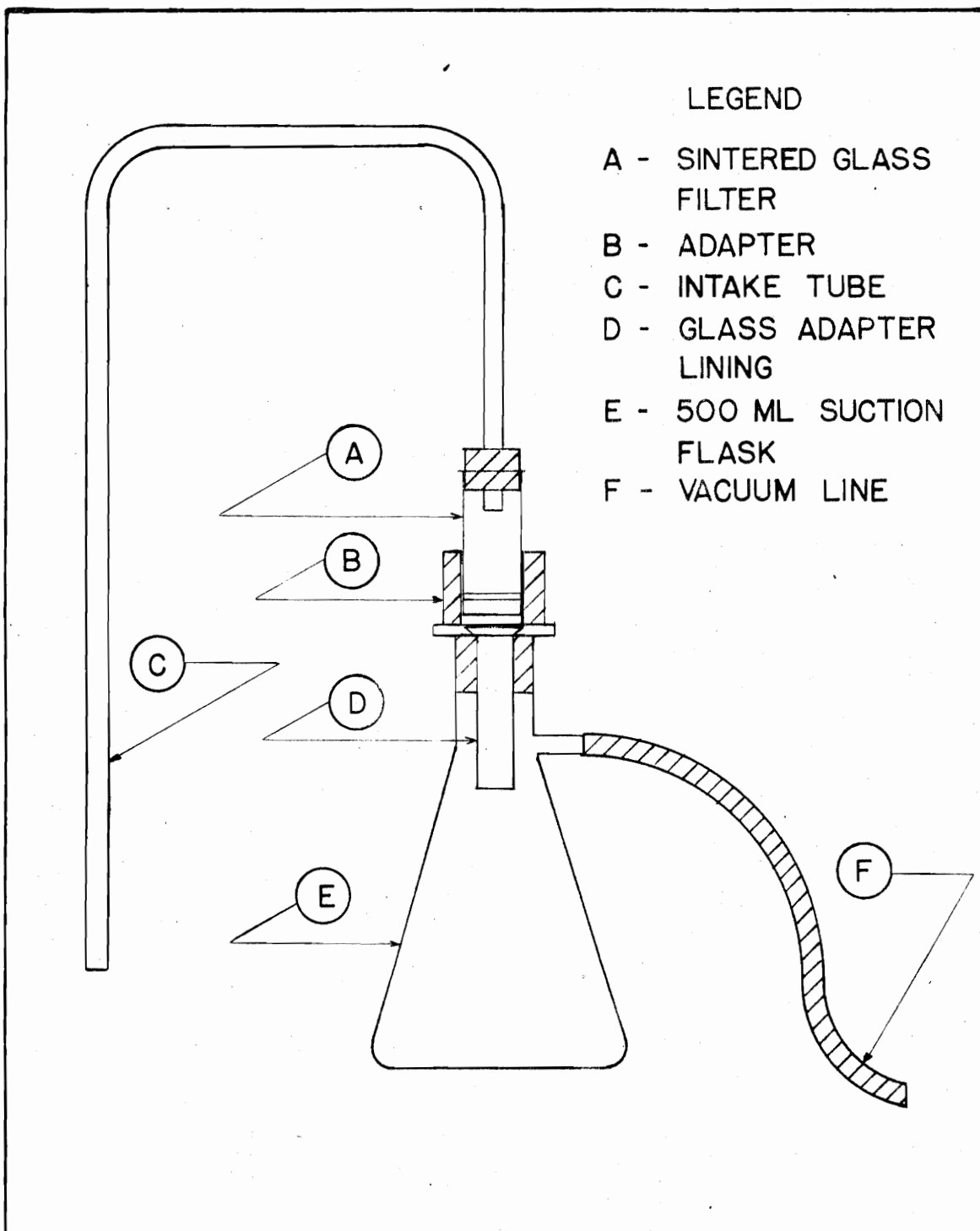


FIGURE 4. APPARATUS FOR THE FILTRATION OF DISUBSTITUTED ALKALI - METAL AMIDES

condensed into the flask for three hours and 25 minutes until all the sodium was dissolved.

An attempt was made to weigh the dimethyl amine added to the reaction. The amine was condensed into a preweighed flask on a balance. The weighed amine was then recondensed into the reaction flask. This method could not be carried out successfully, since the amine evaporating in the weighing flask generated sufficient pressure to rupture all the connections of the apparatus.

An apparatus, shown in Figure 5 on page 67, was assembled to separate the product from the reaction mixture whenever naphthalene had been used in the reaction. A 250-milliliter, roundbottom flask, A, was connected to a 250-milliliter, roundbottom flask, B, with a right angle glass tube, having an inside diameter of 11 millimeters. Flask, B, was provided with a vent. Since flask B was to serve as a condenser, a cold water source, C, was fastened above it, so that the drops of cold water would impinge on the flask and cool it. A large glass funnel, D, was placed under the flask as a catch basin, and the funnel was connected to a drain with rubber tubing.

The reaction mixture was placed into flask A, which was heated in an oil bath. A water pump was connected to vent, E, on the condenser to provide vacuum. Absorbed amine, ether, and naphthalene were distilled off. The solid residue was washed with ether on a sintered glass filter, dried in a stream of nitrogen and bottled under nitrogen.

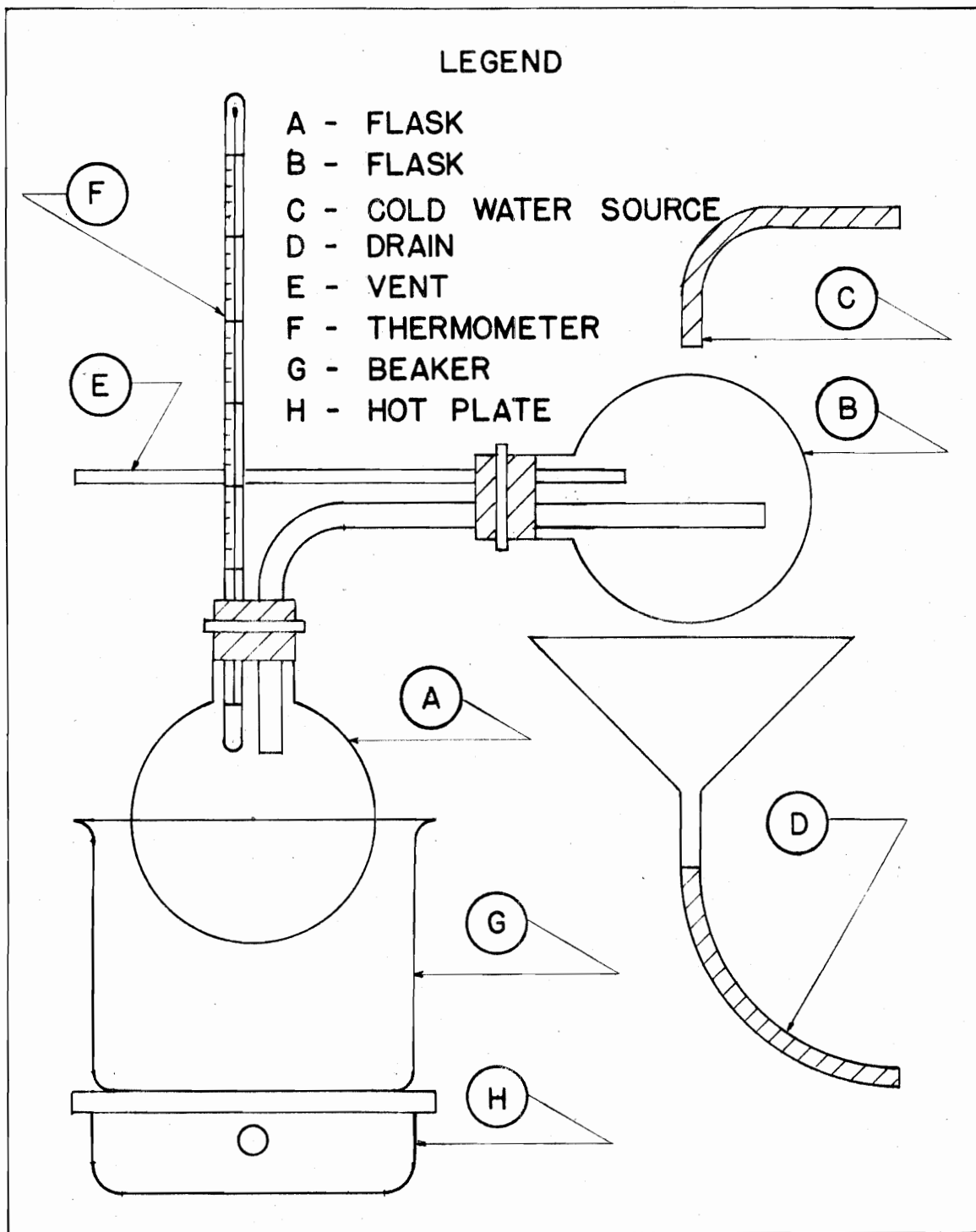


FIGURE 5. APPARATUS FOR THE SEPARATION OF NAPHTHALENE FROM THE REACTION MIXTURE

Preparation of Dimethyl Lithium Amide. The apparatus used in the preparation was the same as the one in Figure 3 on page 63.

The thimble condenser was filled with a mixture of methyl alcohol and dry ice, and the air in the apparatus was replaced with dimethyl amine. To the reaction flask, 3.5 grams (0.5 mol) of lithium shavings were added. Dimethyl amine was condensed upon the lithium for 10 minutes and 1,3 butadiene for five minutes. The two gases were condensed into the reaction flask alternately for five minute periods, until all the lithium metal had dissolved. The reaction mixture then was permitted to warm to room temperature.

The reaction mixture was siphoned into a sintered glass filter, as shown in Figure 4 on page 65. The solid residue was removed from the filter, dried and stored under nitrogen.

The above reaction was repeated with naphthalene instead of 1,3 butadiene. A magnetic stirrer was substituted for the mercury-seal stirrer.

To the reaction flask, 64 grams (0.5 mol) of naphthalene and seven grams (1.0 mol) of cut lithium were added. The volume was made up to one liter with dried ether freshly distilled into the reaction flask. The stirrer was started and a mixture of methyl alcohol and dry ice was placed into the thimble condenser. After the naphthalene had dissolved in the ether, dimethyl amine was condensed into the reaction flask for six hours until all the lithium metal had dissolved.

The reaction mixture was filtered with a sintered glass filter in a dry box. The solid residue was washed with five portions, 50 milliliters each, of dried ether, to remove any naphthalene and dihydronaphthalene. The solid material was then dried and stored under nitrogen.

Preparation of Diethyl Lithium Amide. This preparation was an exact duplication of the reaction set forth in the first example of a patent by Karl Ziegler^(74,75,76,77).

The apparatus shown in Figure 2 on page 60 was modified for this preparation. The heating jacket was removed. Stopper, E, was placed into a side-arm adapter which was fitted to the reaction flask. A trap and a mercury bubbler, in that order, were attached to the side-arm adapter as an exhaust line.

To the flask were added 64 grams (0.5 mol) of naphthalene, 75 grams (1.0 mol) of diethyl amine, seven grams (1.0 mol) of lithium, in five-millimeter cubes, and enough dried ether to make the total volume one liter under nitrogen. The mixture was stirred for three hours and left overnight. The stirring was continued the next day for 10 minutes every two hours until 48 hours had passed. Since no reaction had taken place, the reaction mixture was heated to cause gentle refluxing of the ether. After 10 hours more, all the lithium had dissolved, and the heater and stirrer were turned off.

The reaction mixture was filtered in the apparatus shown in Figure 4 on page 65. The references^(74,75,76,77) predicted that the product would be in solution. Therefore, the filtrate was saved

Almost at once, the filtrate deposited a flocculent precipitate, which was removed with a buchner funnel, and washed with three portions, 100 milliliters each, of benzene.

The above reaction was repeated with the following modifications. A stirring magnet was placed in the flask and a magnetic stirrer under it. The mercury-seal stirrer was replaced with a condenser, which was vented through a drying tube. The apparatus was flushed with nitrogen and the same reagents in the same quantities were added to the flask. The ether used in this reaction was dried and freshly distilled directly into the reaction flask. The stirrer was turned on and left on until all the naphthalene was dissolved in the ether. The stirrer was then replaced with a heating jacket. The reaction mixture was heated so that gentle refluxing took place for 2.5 hours until all the lithium metal was dissolved. The precipitate formed in the reaction was dissolved in 1000 milliliters of benzene.

The benzene solution of the reaction mixture was placed in the apparatus depicted in Figure 5 on page 67. The flask containing the solution was placed in an oil bath, which was placed on a hot plate. The solution was heated until all ether, benzene, naphthalene, and dihydronaphthalene had been distilled off under vacuum. The solid residue was pulverized and stored under nitrogen in a desiccator.

Preparation of Diethyl Sodium Amide. An electrolytic preparation of diethyl sodium amide was attempted. In a standard, ground glass, three-necked, two-liter flask, fitted with a condenser, nitrogen inlet, and exhaust, was placed an ether solution of 75 grams (one mol.) of

diethyl amine. A sodium cathode, a glass tube filled with sodium, and a platinum anode were fitted to the flask and connected to a direct current source. Since the cell would not pass current, this procedure was abandoned and discarded.

Preparation of Naphthyl Alkali-metal Compounds. An attempt to prepare naphthylsodium and naphthyllithium was made in order to study the preparation of disubstituted alkali-metal amides, recommended by Ziegler^(74,75,76,77), in which, as stated in the first example, lithium was reacted with diethyl amine in the presence of naphthalene, dissolved in absolute ether, in a nitrogen atmosphere to form diethyl lithium amide.

Naphthalene was dissolved in 100 milliliters of dry ether and bright sodium chips, measuring 5 x 10 x 10 millimeters, were added in a 250-milliliter erlenmeyer flask, closed to the atmosphere. The amount of sodium used was in a twofold molar ratio to the amount of naphthalene. The reaction was carried out on a 0.078 and 0.1 molar scale based on the expected substitution product of naphthalene. The reactions were allowed to proceed for 24 and 39 hours respectively.

In both cases, a lump of sodium was removed and cut through to determine the extent of the reaction. A sample of the crust and flocculent precipitate was reacted with di-n-butyl amine in dry ether. A sample of the ether was titrated with standard hydrochloric acid, each time, to test for any dissolved naphthylsodium.

The apparatus used in the preparation of naphthyllithium was assembled by fitting a standard, three-necked, 1000-milliliter flask

with a spiral condenser, a mercury-seal stirrer, and a vent connected to a mercury bubbler to exclude air. The stirrer was connected to a variable speed motor with a chuck, and the entire apparatus was flushed with nitrogen. To the flask were added 500 milliliters of dry ether. In the ether 0.5 mol of naphthalene was dissolved. To this were added 1.75 grams of lithium, in pieces measuring 5 x 10 x 10 millimeters. The mixture was stirred for five hours.

The brown flocculent product was separated by filtration, and a portion of the ether solution was titrated with standard hydrochloric acid for the presence of any dissolved naphthyllithium.

Preparation of n-Butyllithium. The apparatus used in the preparation of n-butyllithium is shown in Figure 6 on page 73. A 500-milliliter, ground glass, three-necked flask, A, was fitted with a thermometer well, B, cold thermometer, C, graduated dropping funnel, D, mercury-seal stirrer, E, and adapters F and G. Mercury was placed into the stirrer assembly, E, and a variable speed motor, H, was attached to the stirring rod which was made in the laboratory. To the exhaust vent on adapter, G, a drying tube and a mercury bubbler were attached; to the intake tube a mercury bubbler was attached which was connected with a tank of nitrogen.

The apparatus was flushed with nitrogen, and the flask was placed into a methyl alcohol - dry ice bath. To the flask were added 100 milliliters of dry petroleum ether, and 8.6 grams of lithium chips, measuring 2 x 3 x 5 millimeters, through a paper funnel. A solution of 48 grams (0.5 mol) 1-chlorobutane in 100 milliliters dry petroleum

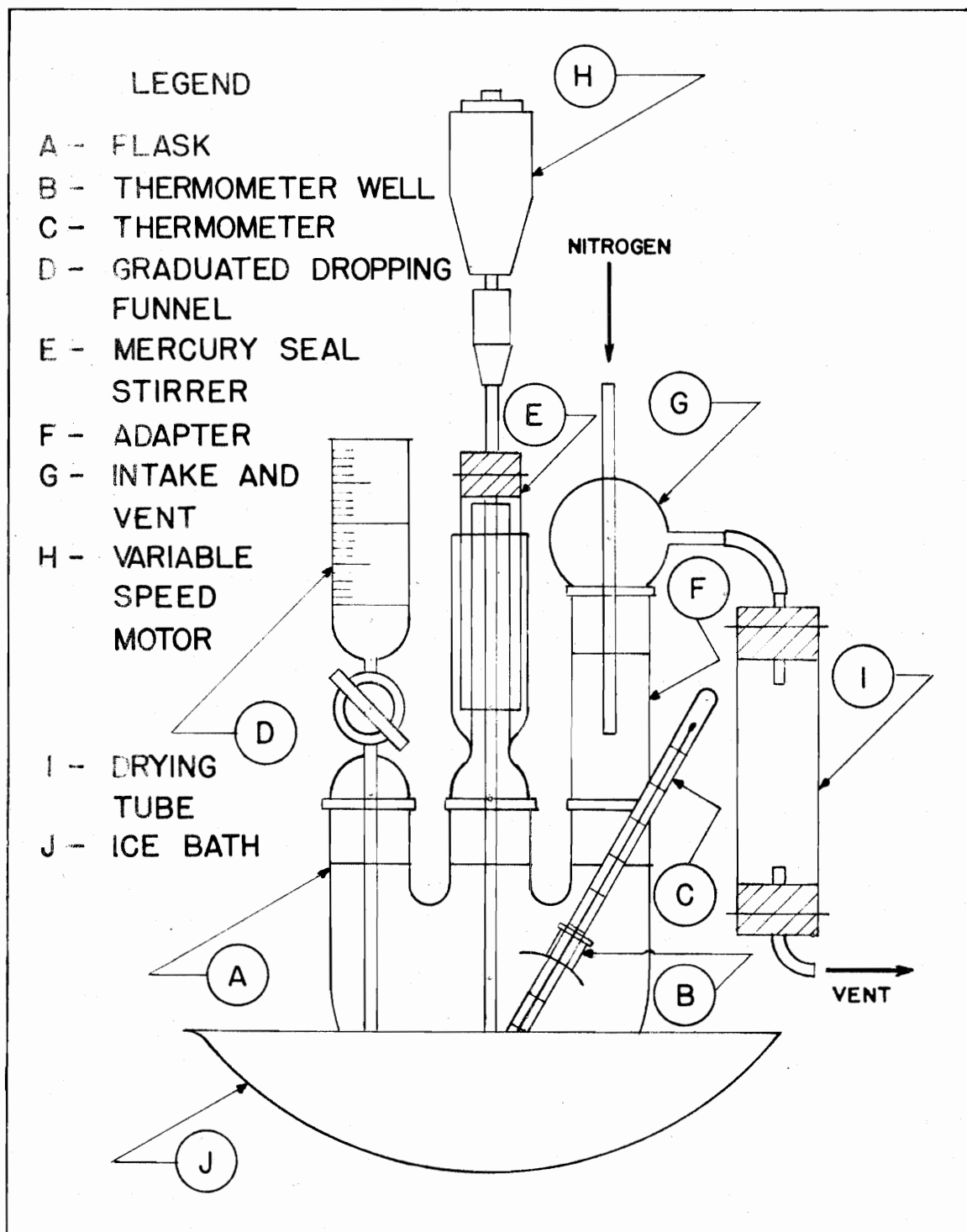


FIGURE 6. APPARATUS FOR THE PREPARATION OF N-BUTYLLITHIUM

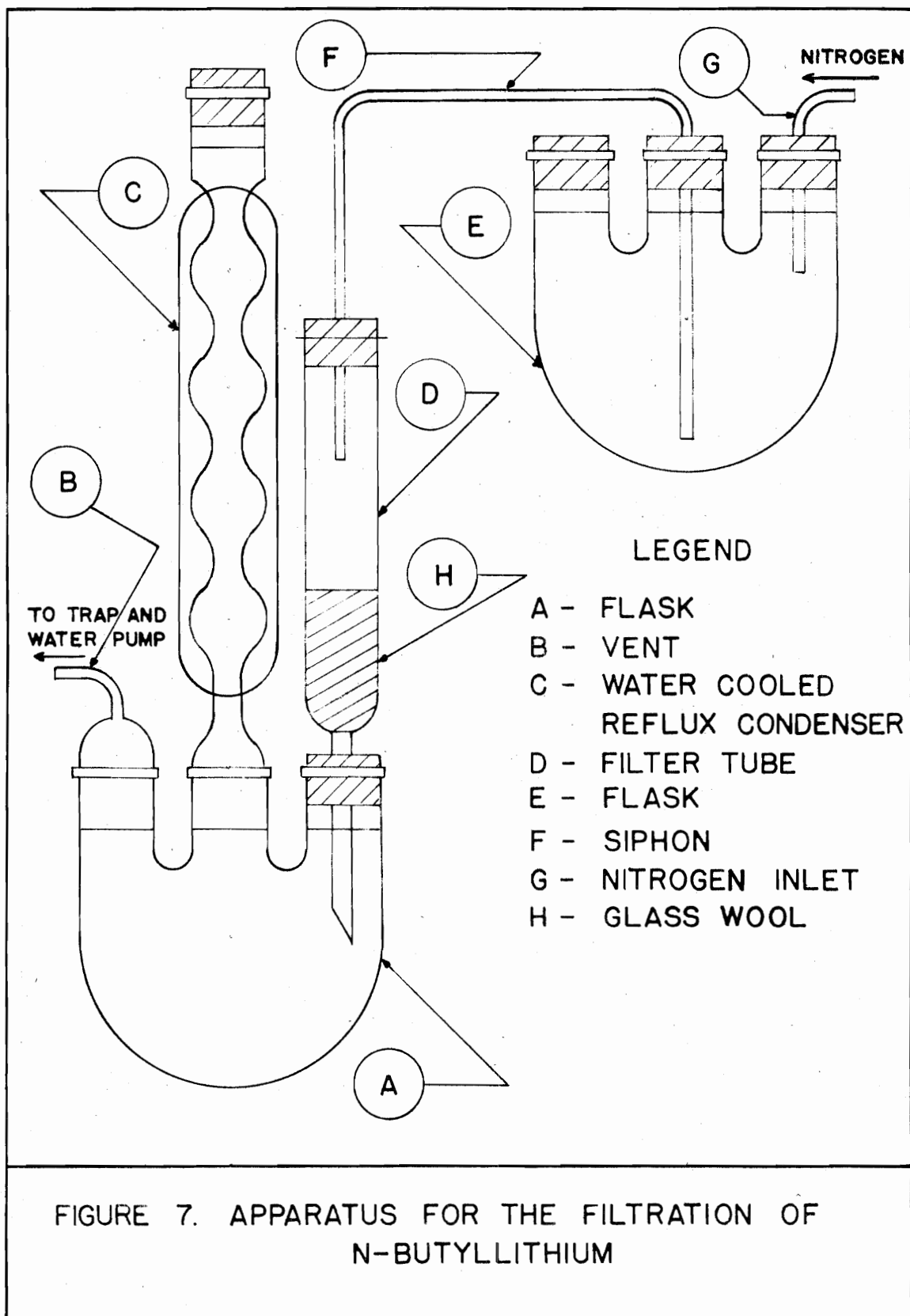
ether was added to the reaction mixture from the graduated dropping funnel at a steady rate for one hour while stirring. Stirring was continued for another hour after the addition of the organic halide was completed. Then the thick precipitate of lithium chloride which had formed during the reaction was allowed to settle, and the apparatus was permitted to attain room temperature, 25 °C, by removing the methyl alcohol - dry ice bath.

The graduated dropping funnel and the mercury-seal stirrer were replaced with rubber stoppers. The vent on adapter, G, was closed.

Filtration of n-Butyllithium Solution. The apparatus used for the filtration of n-butyllithium is shown in Figure 7 on page 75. A standard, ground glass, three-necked 1000-milliliter flask, A, was fitted with an adapter, B, condenser, C, and a six inch filtering tube, D, packed with glass wool for one-third of its length. Adapter B, was connected to a trap, H, and water pump.

The flask used in the preparation of n-butyllithium, E, is connected to the filter, D, with a "U" shaped glass tube siphon, F. The adapters on flask, E, were replaced by nitrogen inlet, G. The entire apparatus was flushed with nitrogen, and a stopper was placed into the top of the condenser. By adjusting the nitrogen pressure at G and the vacuum at B, the n-butyllithium solution was siphoned into the filter, D, and filtered into flask, A.

Filter tube, D, was replaced by a glass inlet tube, the tip of which was immersed in the n-butyllithium solution. The inlet tube was connected to a tank of dimethyl amine through a mercury bubbler. A



stirring magnet was placed into flask, A, and a magnetic stirrer was placed under the flask. The water pump was disconnected from trap, H, and replaced with a mercury bubbler, I, containing 40 millimeters of mercury above the tip of the inlet tube. This bubbler was connected to cause a pressure of 40 millimeters of mercury during the following reaction for the preparation of dimethyl lithium amide.

Preparation of Dimethyl Lithium Amide from n-Butyllithium. The apparatus used in this preparation is the same as the one used for the filtration of n-butyllithium with the modifications described in the preceding paragraph.

The stirrer was started and dimethyl amine was added to the n-butyllithium solution for four hours. Liberated butane escaped through the mercury bubbler. A thick, voluminous, white precipitate was formed. This precipitate formed so rapidly, and was so thick that the amine inlet had to be cleared with wire every 10 minutes, and 100 milliliters of dry petroleum ether had to be added to facilitate stirring. After the reaction was complete dimethyl amine escaped through the bubbler vent.

The amine intake tube was replaced with a stopper, and cold water was passed through the condenser. Mercury was removed from the exhaust bubbler until only 0.5 centimeter of the intake tip was covered. The magnetic stirrer was replaced with a heater, and the stirring magnet was removed with a clean, dry spatula in an effluent stream of nitrogen. The reaction mixture was refluxed for 45 minutes to boil off any ad-

sorbed, excess dimethyl amine. The mixture was then permitted to cool and settle, and 100 milliliters of dry petroleum ether were added.

Determination of Solubility of Dimethyl Lithium Amide. Since dimethyl lithium amide will decompose before it will fuse, an electrolysis of a fused bath was not possible. Therefore, a suitable solvent had to be found for dimethyl lithium amide.

Dimethyl amine and ammonia were chosen as the test solvents. A standard, three-necked, 1000-milliliter flask was fitted with a thimble condenser and a vent guarded with a trap, mercury bubbler, and drying tube. A conductivity cell was constructed to fit the flask, as shown in Figure 8 on page 78. Two pieces of fine platinum wire one-half inch long, A, were sealed half-way into two pieces of thickwalled glass tubing, each six inches long, B. These prepared electrodes were inserted into a rubber stopper, C, one-half inch apart. The electrodes were inserted into a plywood support, D, and two drops of clean mercury were placed into each electrode. The platinum wires were connected to two terminals, E, on the plywood support. The conductivity cell was calibrated with 0.1 normal potassium chloride solution, and was placed in the middle neck of the flask. A stirring magnet was placed into the flask and a magnetic stirrer under the flask.

A sample of analyzed dimethyl lithium amide in petroleum ether suspension was pipetted into the flask. The magnetic stirrer was started and the petroleum ether was distilled off under vacuum at room temperature, 25 °C. The thimble condenser was charged with a

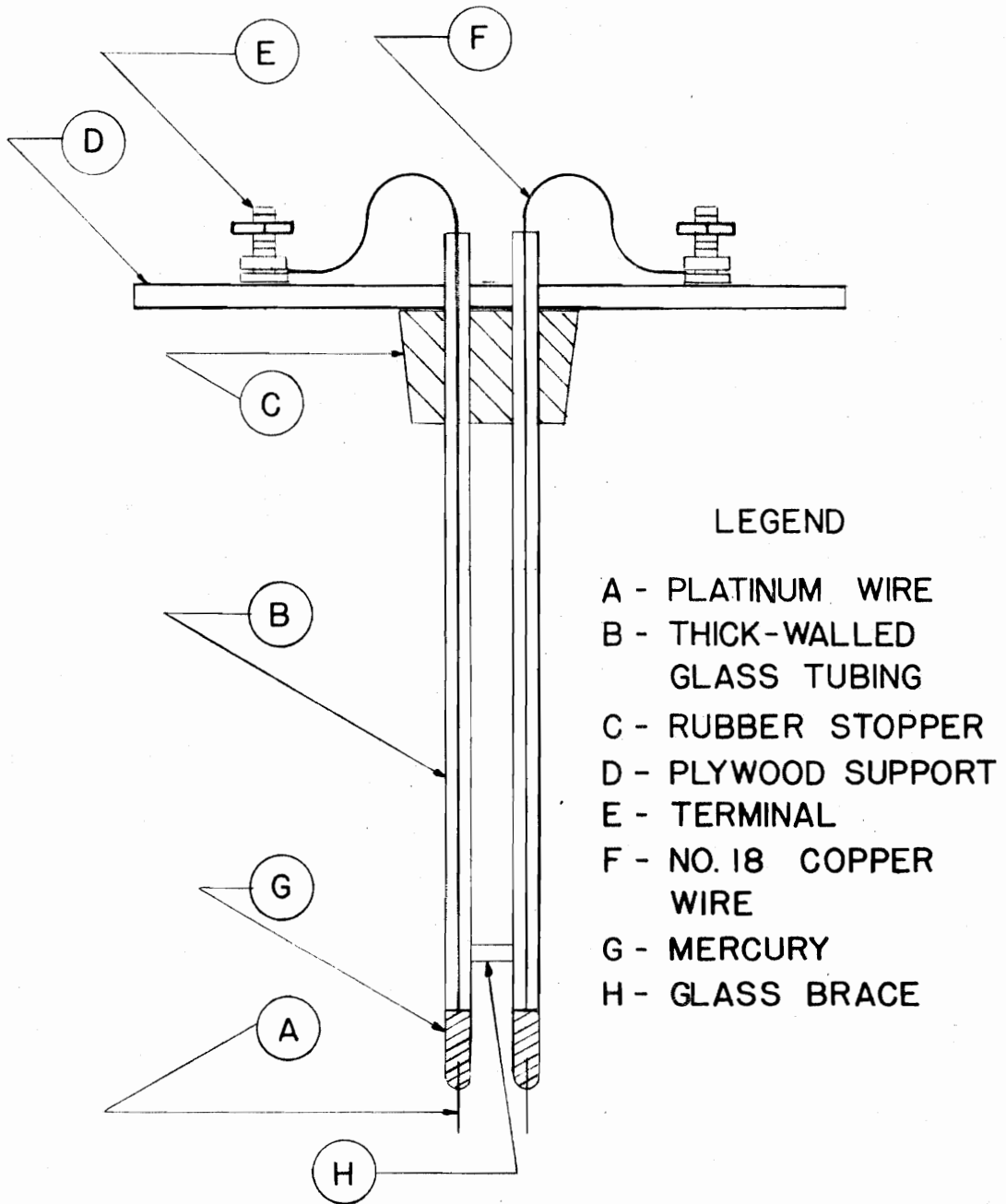


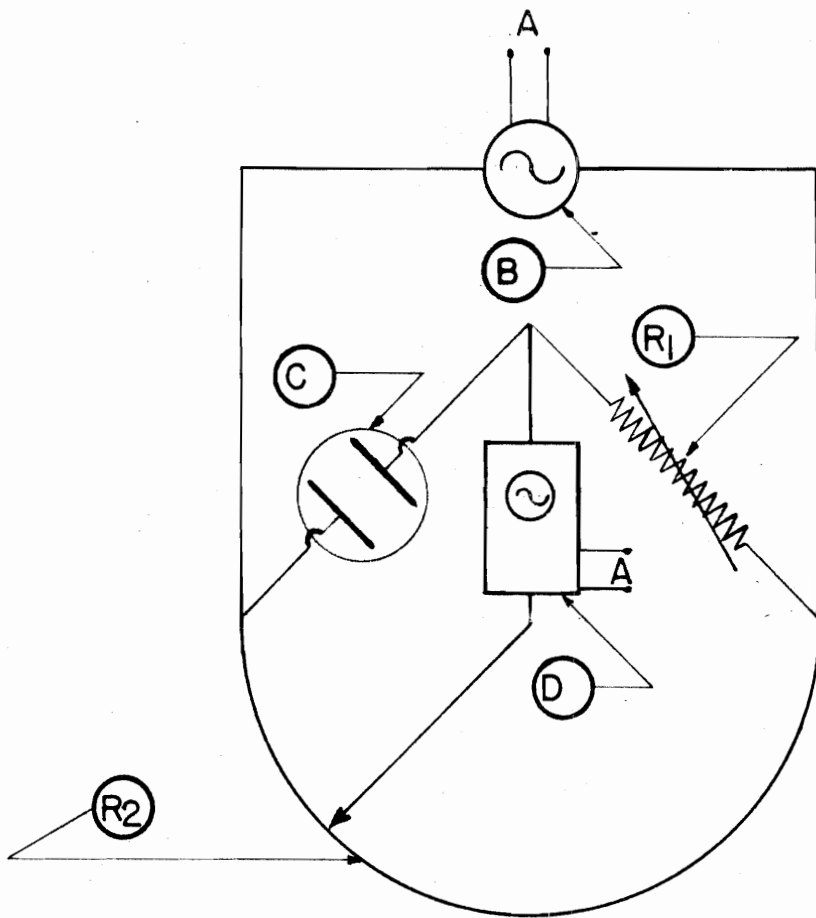
FIGURE 8. CONDUCTIVITY CELL

methyl alcohol - dry ice mixture, and dimethyl amine was condensed into the flask. After the sample of dimethyl lithium amide was covered with solvent and the mixture had been agitated for one hour, the conductivity was measured using a 1000-cycle oscillator, decade resistor and slide wire with an oscilloscope in place of earphones, as shown in Figure 9 on page 80. The preceding procedure was repeated with ammonia as the solvent.

Electrolysis of Dimethyl Lithium Amide. The apparatus used in the electrolysis of dimethyl lithium amide, as shown in Figure 10 on page 81, was assembled as follows. A standard, ground glass, three-necked, 1000-milliliter flask, J, was fitted with a thimble condenser, G, the outlet of which was connected with a mercury bubbler, C. An adapter with a sidearm, H, was fitted to the flask. Sidearm adapter, H, was connected with a trap, R, a mercury trap, S, and a safety trap, T, with rubber tubing.

A gas collection bottle, U, was assembled. A five-gallon carboy was filled with water and fitted with a three-hole stopper. Into the stopper were inserted a vent, W, a siphon drain, X, and a right angle tube, V, which was connected to T with rubber tubing.

The anode, I, was constructed from a platinum flag with a stem sealed to a length of glass tubing. The glass tubing was inserted into a rubber stopper which was inserted into H. The cathode, D, was assembled by sealing a length of chromel wire into glass tubing so that 10 millimeters of the wire protruded. The glass tubing was inserted in a rubber stopper and placed into the middle neck of flask J.



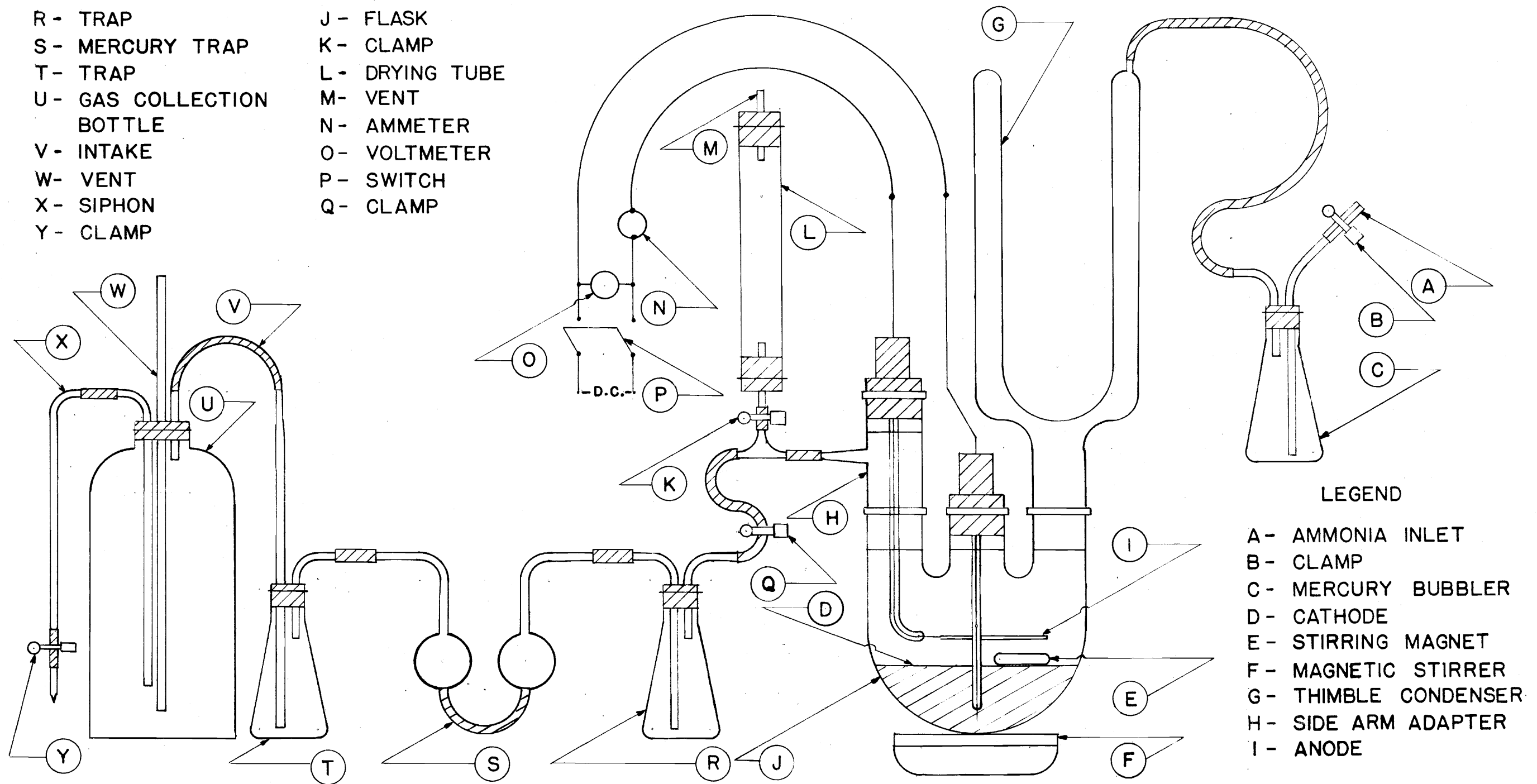
LEGEND

- A - A.C. 110 V 60 CYCLES SOURCE
- B - OSCILLATOR
- C - CONDUCTIVITY CELL
- D - OSCILLOSCOPE
- R₁ - DECADE RESISTANCE BOX
- R₂ - SLIDE WIRE RESISTANCE

FIGURE 9. CIRCUIT DIAGRAM FOR MEASURING CONDUCTIVITY

R - TRAP
 S - MERCURY TRAP
 T - TRAP
 U - GAS COLLECTION
 BOTTLE
 V - INTAKE
 W - VENT
 X - SIPHON
 Y - CLAMP

J - FLASK
 K - CLAMP
 L - DRYING TUBE
 M - VENT
 N - AMMETER
 O - VOLTMETER
 P - SWITCH
 Q - CLAMP



LEGEND

A - AMMONIA INLET
 B - CLAMP
 C - MERCURY BUBBLER
 D - CATHODE
 E - STIRRING MAGNET
 F - MAGNETIC STIRRER
 G - THIMBLE CONDENSER
 H - SIDE ARM ADAPTER
 I - ANODE

FIGURE 10. APPARATUS FOR THE ELECTROLYSIS OF DIMETHYL LITHIUM AMIDE
 IN AMMONIA

The platinum anode and chromel cathode wire were connected to a double knife switch, P, with copper bell wire. An ammeter, N, was connected into the wire between the anode and the switch. A voltmeter, Q, was connected between the anode and cathode wire. The switch, P, was connected with a direct current generator.

Into flask, J, 200 milliliters of clean, dry mercury were placed, and a stirring magnet was floated on the mercury. A magnetic stirrer, F, was placed under the flask. The chromel cathode was lowered into the mercury and the anode was adjusted so that the platinum flag was parallel to and one and one-half inches above the surface of the mercury. The entire apparatus was flushed with nitrogen.

Approximately one-sixth of a mol of dimethyl lithium amide in a petroleum ether suspension was withdrawn from its container with a pipet and pipettor, and transferred to flask, J. Screw clamp, Q, and B, were closed, and screw clamp, K, was opened. Vacuum was applied at M with a water pump until all the petroleum ether had been removed from flask, J. Screw clamp K was closed and B opened.

Into the thimble condenser, 600 milliliters of acetone were placed and small pieces of dry ice were added until all vigorous bubbling had ceased. Then, the condenser was filled with dry ice. The valve on the ammonia cylinder was opened, screw clamp, Q, was opened, the magnetic stirrer was started, and ammonia was condensed into the flask until it covered the platinum anode by one-half inch.

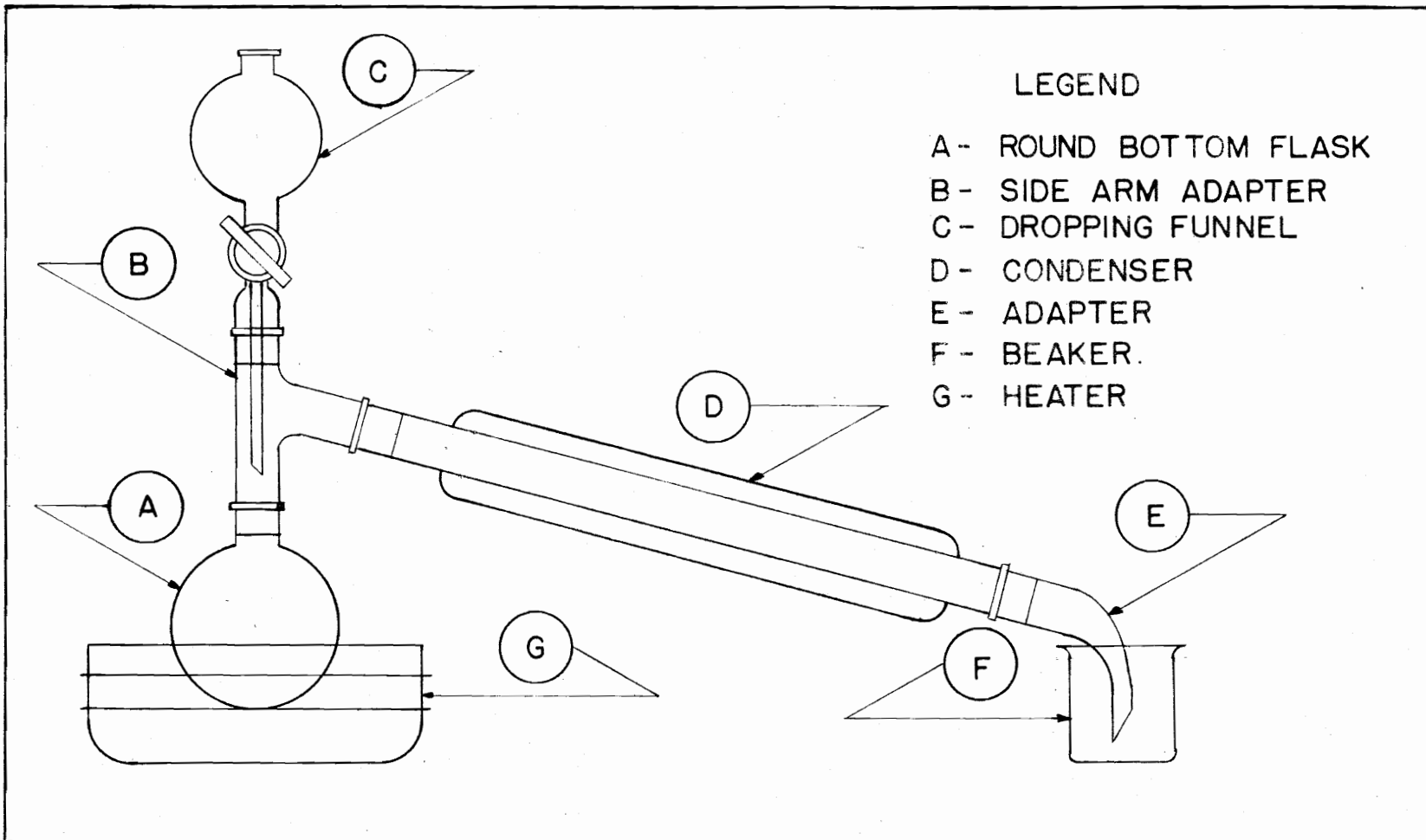
The direct current generator was started, and switch, P, was closed. Dry ice was added to the thimble condenser whenever it was

necessary. The electrolysis was continued until approximately 10,000 coulombs had passed into the reaction. No water insoluble gas was released by the reaction.

After the electrolysis was completed, switch, P, was opened, and the direct current generator was stopped. The ammonia layer was decanted from the mercury cathode into a 250-milliliter erlenmeyer flask, fitted with a drying tube and mercury bubbler. The ammonia was permitted to boil off overnight, and 1.5 to 2.5 milliliters clear, waterwhite, viscous liquid remained in the flask as the product.

Quantitative Analysis for Organo Lithium Compounds. Since the organo lithium compounds were prepared in petroleum ether, the lithium halide, also formed, was insoluble. The organolithium compound - petroleum ether solution was decanted from the reaction mixture and filtered through glass wool. A one milliliter aliquot of the filtered solution was hydrolyzed with 10 milliliters distilled water and titrated with standard hydrochloric acid to the phenolphthalein end point. The milliequivalents of hydrochloric acid used are equal to the milliequivalents organo lithium compound in the aliquot portion.

Quantitative Analysis for Amine Content. The apparatus shown in Figure 11 on page 84 was assembled. A 100-milliliter, ground glass, round-bottom flask, A, was fitted with a side arm adapter, B, which was fitted with a dropping funnel, C, and a water cooled condenser, D. An adapter, E, was attached to the condenser. A 250-milliliter beaker, F, was placed under adapter E, and flask A was set into heater, G. A ground glass thermometer was fitted with an adapter so that it could



LEGEND

- A- ROUND BOTTOM FLASK
- B- SIDE ARM ADAPTER
- C- DROPPING FUNNEL
- D- CONDENSER
- E- ADAPTER
- F- BEAKER.
- G- HEATER

FIGURE 11. APPARATUS FOR AMINE ANALYSIS OF AMIDES

be used to replace the dropping funnel C. Standard solutions of hydrochloric acid and sodium hydroxide were prepared.

If the sample to be analyzed was dry and in powder form, a portion was weighed on an analytical balance and placed into flask A, after 25 milliliters of standard hydrochloric acid had been pipetted in beaker F and diluted with distilled water until the liquid covered the tip of adapter E. The sample in flask A was hydrolyzed with 25 milliliters of distilled water and 10 milliliters of 20 per cent sodium hydroxide solution, added from the dropping funnel. Any amine liberated by the hydrolysis was absorbed by the hydrochloric acid in beaker F. The contents of flask A were heated until the water refluxed, to drive off any remaining dissolved or absorbed amine. As the flask was cooled care was taken that though the adapter tip remained covered with acid solution, none was drawn into the apparatus.

The contents of beaker F, hydrochloric acid solution and any absorbed amine, were titrated with standard sodium hydroxide solution to the phenolphthalein end point. From this data the percentage of amine in the sample could be calculated.

If the sample to be analyzed was highly reactive and sensitive to air and moisture, such as dimethyl lithium amide, some decomposition would have occurred during weighing and handling involved. Therefore, the sample was removed from the reaction flask in its ether suspension and transferred to flask A with a pipet and pipettor. In this case 25 milliliters of distilled water were sufficient to hydrolyze the sample. As above, any liberated amine was captured by the hydrochloric acid

solution in the receiver F. The contents of flask A were heated to drive off all the amine. The ether distilled off also, but it was inert to the reagents used in the analysis. As above, the contents of the receiver were titrated and the milliequivalents of amine present were calculated. Then the residue in flask A was titrated as lithium hydroxide, with standard hydrochloric acid solution to the phenolphthalein end point. From this data, the per cent of amine and of amide in the sample were calculated.

Quantitative Analysis for Alkali-metals. A gravimetric method was used to analyze for sodium or lithium.

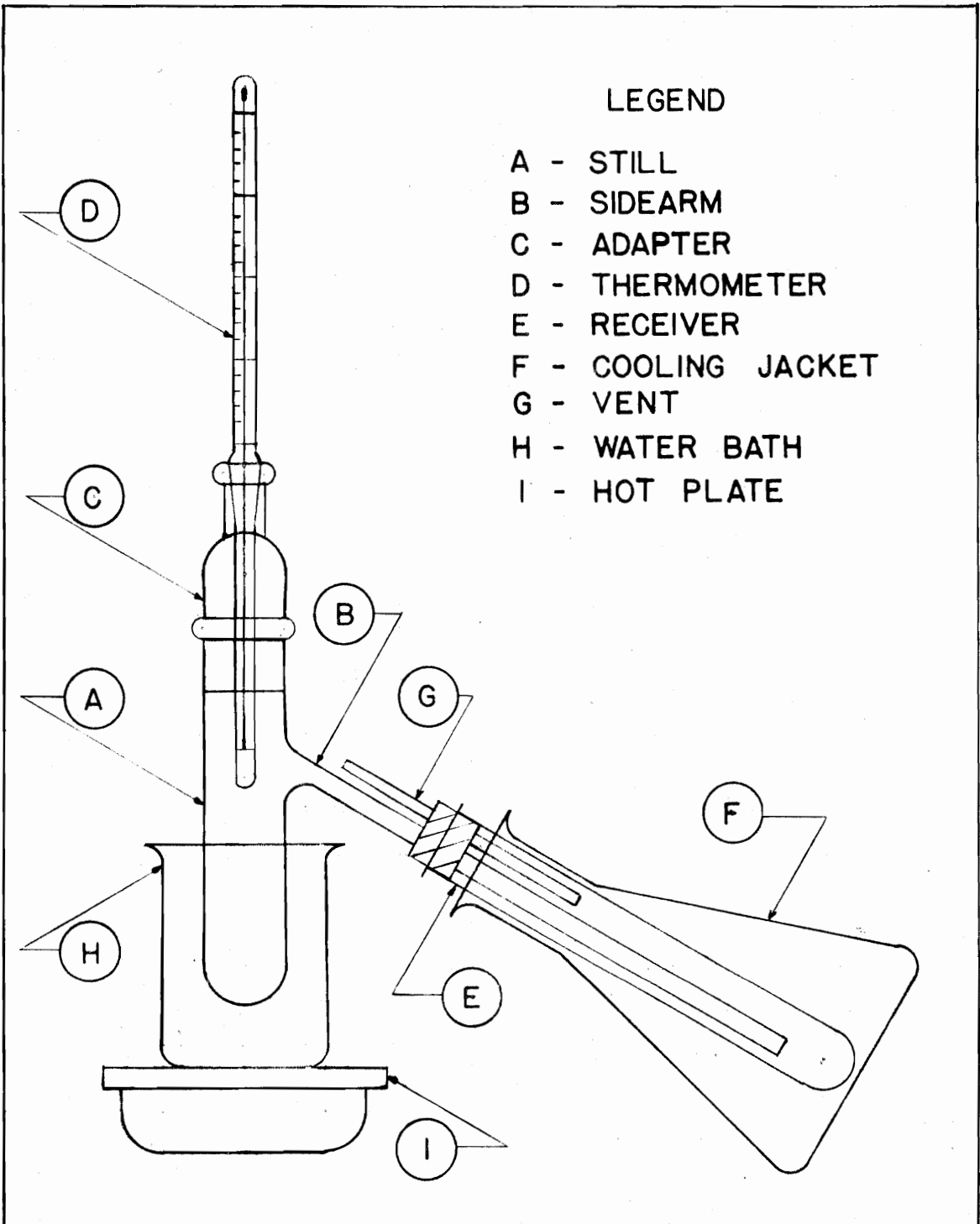
Two crucibles and covers were ignited in the flame of a bunsen burner, cooled in a desiccator, and weighed on an analytical balance to a constant weight. A weighed sample was placed in each crucible, and hydrolyzed with three milliliters of distilled water. The samples were heated until dry, and one milliliter of 20 per cent sulfuric acid solution were added. The tops were placed, at an angle, on the crucibles to prevent spattering, but permit all volatile matter to escape to the atmosphere. The crucibles were heated gently until all volatile matter had been removed, and then the tops were removed. Both the tops and crucibles were ignited. After the crucibles had been cooled in a desiccator, the sulfuric acid treatment was repeated. The crucibles and tops were reignited and cooled until they attained a constant weight. The residue was considered to be alkali-metal sulfate. From this data the amount of alkali-metal in the sample was calculated.

Determination of Melting Points. Melting points of solids were determined by the well known capillary tube method, using a -10 to 360 °C thermometer in a 250-milliliter glycerine bath, which was heated 2 °C per minute.

Determination of the Boiling Point. The boiling point of liquids in quantities smaller than five milliliters was determined with the apparatus shown in Figure 12 on page 88. A female, 24/40, ground glass joint, A, was sealed shut at one end. A piece of glass tubing, B, four inches long, having an inside diameter of 6 millimeters, was sealed to the side of A, one inch below the ground glass joint at an angle of 30 degrees below horizontal. A ground glass adapter, C, was fitted to A, and a ground glass thermometer was inserted. A five-inch test tube, E, was attached to B as a receiver. A 500-milliliter erlenmeyer flask, F, was placed over E as a cooling jacket. The receiver was supplied with a vent, G.

The liquid sample was placed into A, which was immersed in a water-filled 150-milliliter beaker, H. The beaker was placed on a hotplate, I. Crushed ice was placed in cooling jacket F. The unknown liquid was heated at the rate of one degree every two minutes from 37 °C. A considerable amount of refluxing occurred due to vapors rising past the side arm opening into adapter C and condensing back into A. The temperature at which the liquid distilled over was recorded as the boiling point.

Determination of the Specific Gravity. This method is suitable for quantities of liquids smaller than two milliliters. A pycnometer⁽⁵⁴⁾



LEGEND

- A - STILL
- B - SIDEARM
- C - ADAPTER
- D - THERMOMETER
- E - RECEIVER
- F - COOLING JACKET
- G - VENT
- H - WATER BATH
- I - HOT PLATE

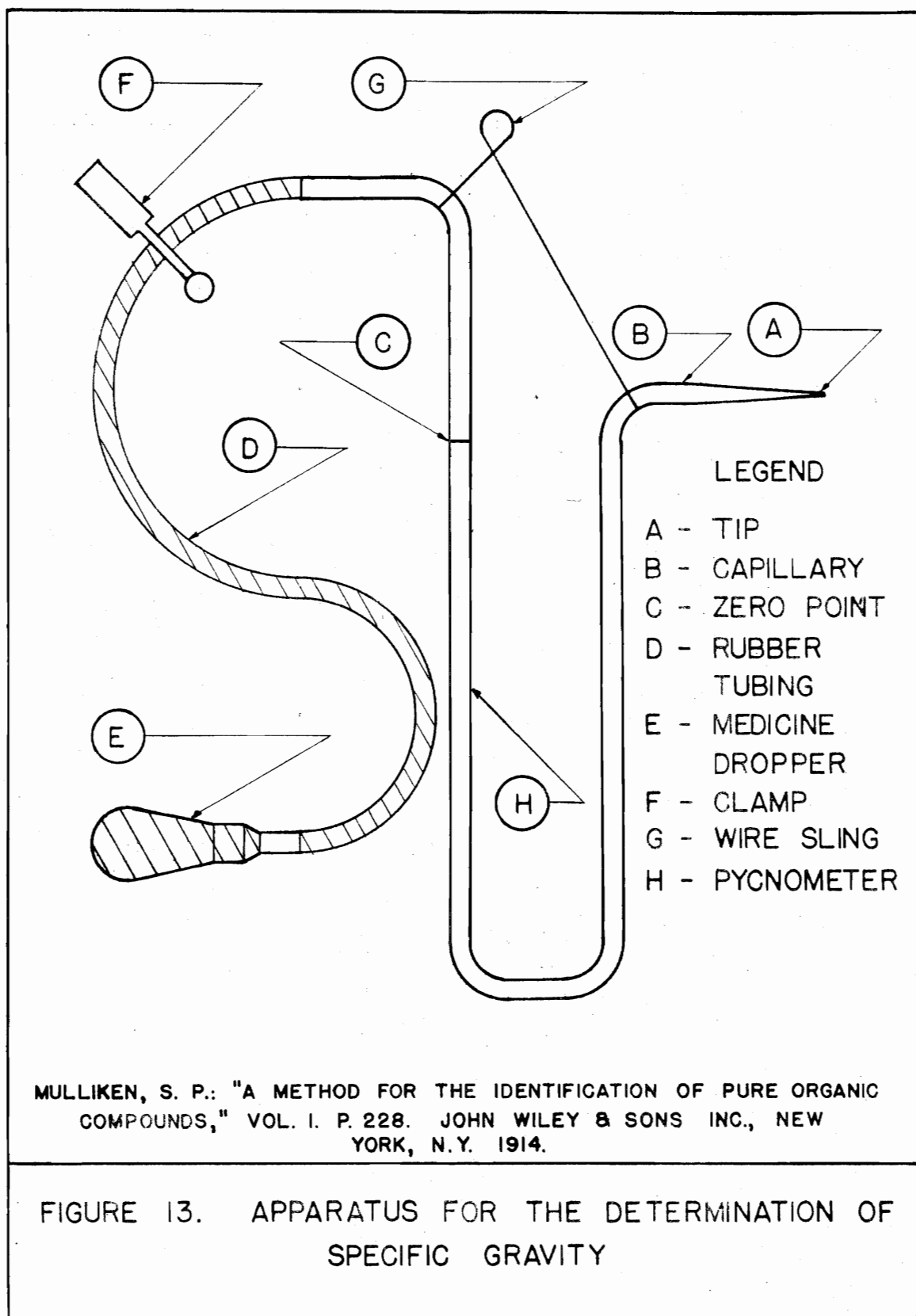
FIGURE 12. APPARATUS FOR THE DETERMINATION OF BOILING POINTS

was prepared from 28-30 centimeters of thick walled glass tubing, having an inside diameter of one millimeter and an outside diameter of five millimeters. The glass tubing was bent into a "U" shape as shown in Figure 13 on page 90. The section of glass tubing from B to A was drawn out to a thick walled capillary eight centimeters long. A horizontal line, C, was marked on the tubing as the zero point. A short length of rubber tubing, D, was attached, and a medicine dropper, E, was inserted in the free end of the rubber tubing. A clamp, F, was placed on the rubber tubing near the point of attachment to the pycnometer. To calibrate the pycnometer cold water was drawn above the scribed line, C, by flexing the bulb of the dropper. Clamp, F, was put in place. The dropper, E, and tube, D, were detached. The pycnometer and contents were permitted to attain room temperature, 25 °C. Dry filter paper was touched to tip, A, until the liquid level was at line, C. The pycnometer was weighed by hanging it on the hook above the platform on an analytical balance by wire sling, G.

The above process was repeated with the unknown liquid. The specific gravity was determined by dividing the weight of the unknown by the weight of the water.

Determination of Acid Soluble Content. A water suspension of asbestos fibers was poured into four clean gooch crucibles to form a filter mat. The crucibles were then dried in an oven at 125 °C to constant weight, and cooled in a desiccator.

A weighed sample was placed in each crucible. The crucibles were placed on a suction flask with a rubber adapter. The flask was con-



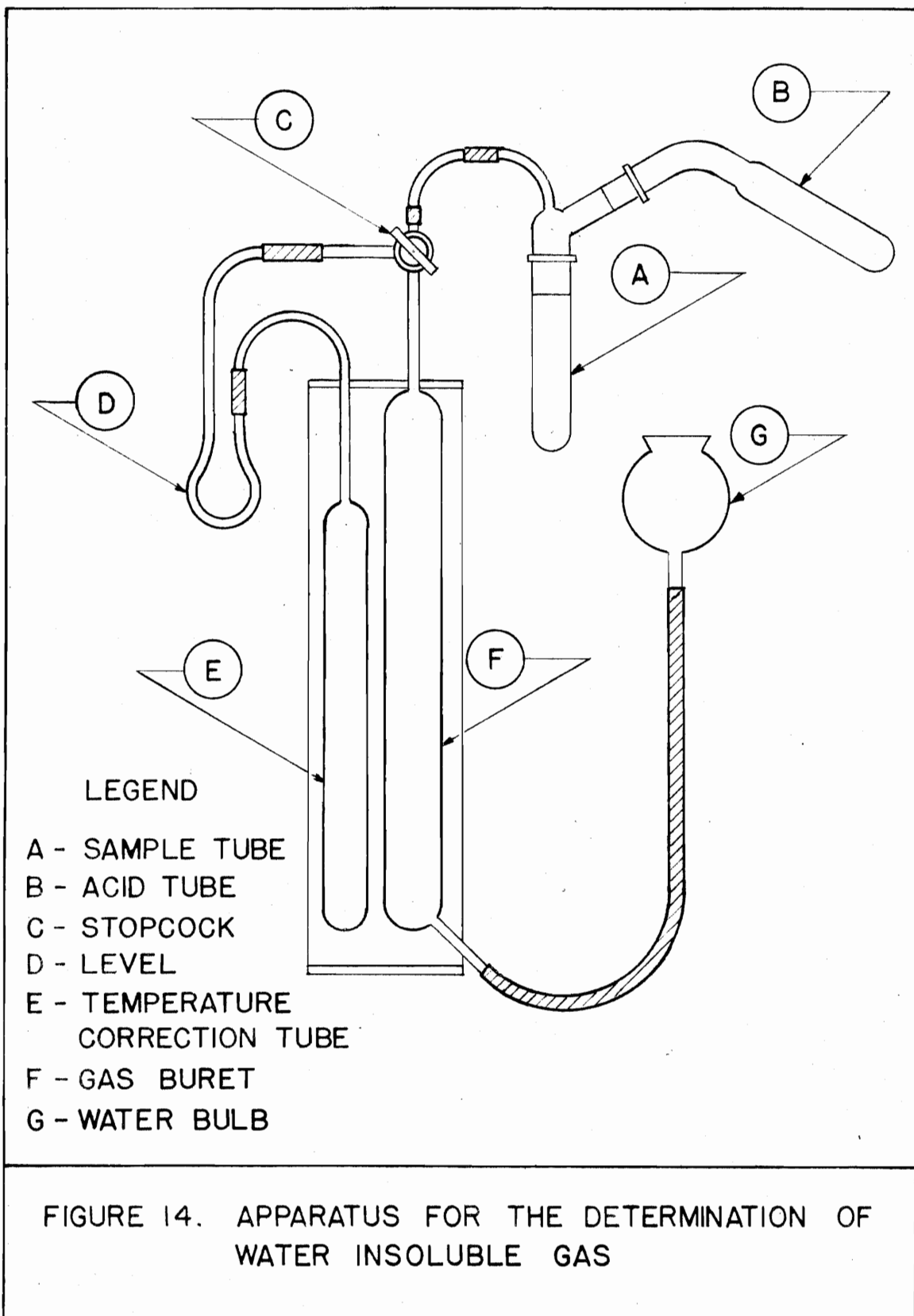
ected to a water pump. The samples were washed with five 50-milliliter portions of 1:1 hydrochloric acid solution and two 50-milliliter portions of distilled water. The samples were then dried in an oven at 125 °C for four hours until each crucible attained constant weight.

Determination of Water Insoluble Gas Content. Due to the deterioration and loss of nitrogen content undergone by some of the prepared materials, a determination of water insoluble gas content was made by use of the active hydrogen apparatus, Figure 14 on page 92.

The sample tube, A, was weighed dry, and then weighed again with the sample in it. Approximately 15 milliliters of a 1:1 hydrochloric acid solution were poured into acid tube, B. The water level in gas buret, F, was adjusted to zero and in the arms of level, D, the water level was adjusted to even height, by raising the water bulb, G, with stopcock, C, closed to the sample tube. Stopcock, C, was opened to the sample tube with the water level in F at zero. Acid was added to the sample carefully by inverting acid tube, B. The sample tube was warmed until all evolution of gas had ceased. The system was allowed to cool and the stopcock was closed to the sample tube. The water bulb was adjusted until water in both arms of D rose to an even height. The scale on the gas buret was read at the water level as the volume of gas evolved. The atmospheric pressure and the temperature were recorded.

Determination of Equivalent Weight by Electrometric Titration.

A weighed sample of the unknown material was placed into a 250-milliliter

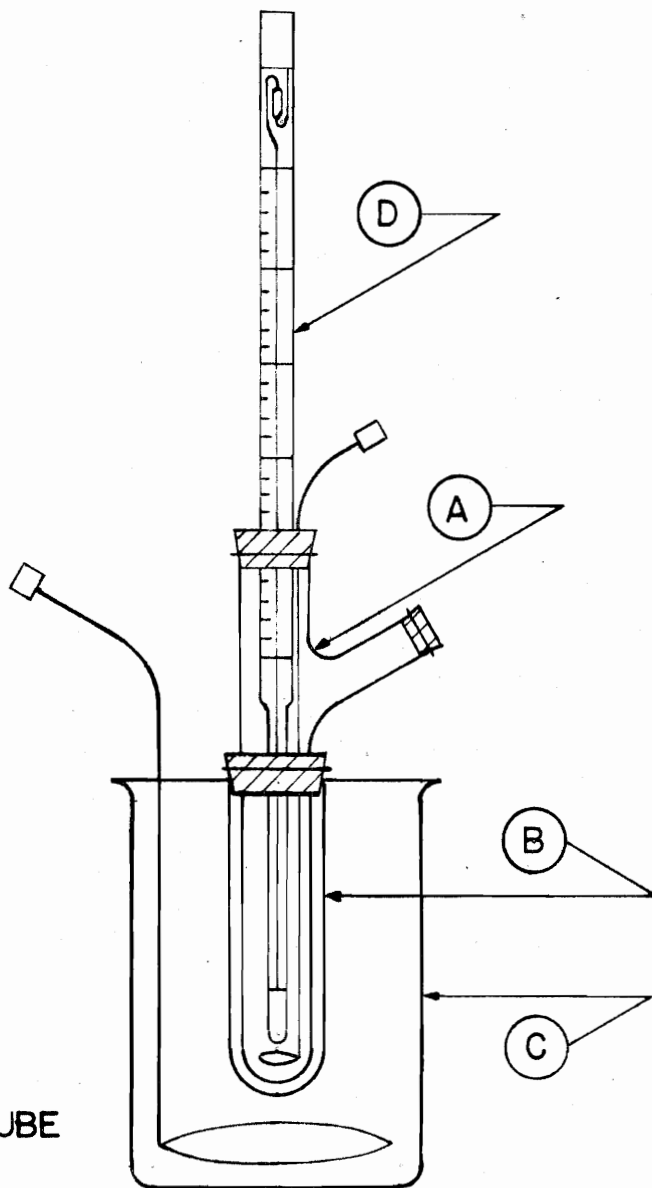


beaker. Distilled water was added to make a volume of 75 milliliters. A stirring magnet was placed into the beaker. The beaker was placed on a magnetic stirrer, and the electrodes of a Beckman pH Meter were immersed in the mixture. The pH meter was calibrated, and a reading was taken. Standard hydrochloric acid solution was added to the mixture from a buret in five-milliliter portions. The contents of the beaker were mixed and the meter was read after each addition of hydrochloric acid solution. Data was plotted and the equivalent weight calculated.

Determination of Molecular Weight by Depression of the Freezing Point of Benzene. As a check on the molecular weight determination by titration, the freezing point method was used.

A weight of 12.9 grams, of pure benzene was placed in the tube, A, Figure 15 on page 94, with a Beckmann thermometer, D, and a stirrer. The tube A, was fitted inside another, B, leaving an air space between, and the whole assembly was immersed in a covered vessel, C, containing a freezing mixture of crushed ice and chromate brine. The temperature of the benzene was allowed to fall until it was about 0.5° below its normal freezing point, 5.51°C (56). It was supercooled without solid separating. Vigorous stirring then caused crystallization to commence, and the temperature rose to the freezing point, which was recorded.

The tube, A, was then removed, warmed slightly to melt the solid, and a weighed amount of sample was added and allowed to dissolve. The freezing point of the solution was determined by the same method as



LEGEND

- A - SAMPLE TUBE
- B - JACKET
- C - COVERED VESSEL
- D - BECKMANN THERMOMETER

GLASSTONE, S.: "TEXTBOOK OF PHYSICAL CHEMISTRY," P. 646.
D. VAN NOSTRAND CO., INC., NEW YORK, N.Y. 1948. 2 ED.

FIGURE 15. BECKMANN FREEZING POINT APPARATUS

for the solvent, and the difference was the depression of the freezing point. Sufficient data were then available for the molecular weight of the solute to be evaluated.

Data and Results

The data obtained during the course of this investigation and the results observed and calculated from the data are presented in tabular form in the following section.

Preparation of Disubstituted Alkali-metal Amides. The data observed during the investigation of the direct method for the preparation of disubstituted alkali-metal amides developed by Ziegler^(74,75,76,77) are listed in Table VII on page 96.

The product of preparation number nine in Table VII on page 96 was subjected to a determination of water insoluble gas evolved, the results of which are listed in Table VIII on page 97. The product was also analyzed for acid soluble content. The data from this determination are listed in Table IX on page 98.

Preparation of Naphthyl Alkali-metal Compounds. The preparation of naphthyllithium and naphthylsodium was attempted in an effort to investigate the preceding preparation, and the data collected during these attempts are listed in Table X on page 99.

Preparation of n-Butyllithium. The data derived from the four preparations of n-butyllithium are listed in Table XI on page 100.

TABLE VII

Preparation of Disubstituted Alkali-metal Amides

| Run No | Preparation | Reagents | | | | | | | | | | Conditions | | | Analysis ^a | | | | | | |
|-----------|-------------------------|-----------------|--------------|-------------|------------|--------------------------|-------------|---------------|--------------|-----------------|--------------------|------------|------------|-----------------------|-----------------------|--------|--------------------|-------------|---------|-----------|------------|
| | | Alkali-metal | | Amine | | Hydrocarbon ^b | | Solvent | | Atmos- phere | Temp °C | Time hr | Amine % | Metal % | C % | H % | N % | | | | |
| | | Metal | Weight gm | Mols mol | Amine | Weight gm | Mols mol | Hydrocarbon | Weight gm | | | | | | | | | Mols mol | Solvent | Vol ml | Mol equ |
| 1 | Di-n-butyl sodium amide | Na | 15.0 | 0.66 | di-n-butyl | 32.5 | 0.25 | naphthalene | 32.1 | 0.25 | ether ^c | 850 | 8.20 | nitrogen ^d | 25 | 3.25 | 73.9 | 18.9 | | | |
| 2 | Dimethyl sodium amide | Na | 1.4 | 0.16 | dimethyl | | | 1,3 butadiene | | | none | ... | | amine | -3 | 19.0 | 58.8 | 30.8 | | | |
| 3 | Dimethyl sodium amide | Na ^e | 12.0 | 0.50 | dimethyl | | | 1,3 butadiene | | | toluene | 500 | 4.70 | nitrogen ^f | -3 | 14.0 | ^g | | | | |
| 4 | Dimethyl sodium amide | Na | 22.5 | 1.0 | dimethyl | | | 1,3 butadiene | | | none | ... | | nitrogen | -3 | 12.0 | ^h | | | | |
| 5 | Dimethyl sodium amide | Na | 23.0 | 1.0 | dimethyl | | | naphthalene | 64.0 | 0.50 | ether ⁱ | 850 | 8.20 | nitrogen | 7 | 3.5 | 3.0 | 30.2 | 17.50 | 3.77 | 0.96 |
| 6 | Dimethyl lithium amide | Li | 3.5 | 0.5 | dimethyl | | | 1,3 butadiene | | | none | ... | | amine | -3 | 3.0 | ^j | | | | |
| 7 | Dimethyl lithium amide | Li | 7.0 | 1.0 | dimethyl | | | naphthalene | 64.0 | 0.50 | ether ^k | 850 | 8.20 | nitrogen | 7 | 6.0 | 9.3 | 13.9 | 38.72 | 7.20 | 2.90 |
| 8 | Diethyl lithium amide | Li | 7.0 | 1.0 | diethyl | 75.0 | 1.00 | naphthalene | 64.0 | 0.50 | ether ^l | 850 | 8.20 | nitrogen | 35 | 10.0 | ^m | | | | |
| 9 | Diethyl lithium amide | Li | 7.0 | 1.0 | diethyl | 75.0 | 1.00 | naphthalene | 64.0 | 0.50 | ether ⁱ | 850 | 8.20 | nitrogen | 35 | 2.5 | 58.0 | 20.15 | 18.33 | 3.86 | 1.60 |
| 10 | Diethyl sodium amide | Na | ... | ... | diethyl | 75.0 | 1.00 | none | | | ether ^k | 1000 | 9.65 | nitrogen | 25 | 0.0 | ^h | | | | |

^a The analysis for amine and alkali-metal content was done in the laboratory, as described previously. The elemental analyses were done by Micro-Tech Laboratories, Skokie, Ill. The amine and alkali-metal contents of the theoretical products are as follows: Di-n-butyl sodium amide, 84.78 % and 15.22 %; dimethyl sodium amide, 65.70 % and 34.30 %; dimethyl lithium amide, 86.29 % and 13.71 %; diethyl lithium amide, 91.15 % and 8.85 %; and diethyl sodium amide, 75.80 % and 24.20 % respectively.

^b The hydrocarbons used in the reactions contained conjugated double bonds, and they acted as carriers for the alkali-metals.

^c The ether was taken from an opened container.

^d The nitrogen was water pumped.

^e The sodium was in the form of a high surface dispersion in toluene.

^f This nitrogen and that used in all subsequent reactions was oil pumped.

^g A tar like product was obtained which could not be separated for analysis.

^h No reaction occurred.

ⁱ The ether was freshly distilled into the reaction flask.

^j The quantity of product obtained was insufficient for analysis.

^k The ether was dried with sodium hydride and distilled into the reaction flask.

^l The ether was taken from a container labeled dry ether.

^m The product obtained in this reaction was similar to lithium nitride, and upon hydrolysis with distilled water an ammonia like gas was liberated.

TABLE VIII

Determination of Water Insoluble Gas Evolved from Product
of Attempt to Prepare Dimethyl Lithium Amide

Samples of preparation No 9 in Table VII on page 96 were hydrolyzed with 1:1 hydrochloric acid.

| | Test | | |
|-----------------------------|--------|--------|--------|
| | 1 | 2 | 3 |
| Weight of sample | 0.0708 | 0.1501 | 0.1237 |
| Volume of gas liberated | 2.3 | 8.9 | 4.6 |
| Temperature | 25.0 | 25.0 | 25.5 |
| Barometric pressure | 709.3 | 707.5 | 711.3 |
| Vapor pressure of water | 23.8 | 23.8 | 24.5 |
| Gas per sample ^a | 0.0118 | 0.0218 | 0.0137 |

^a The gas content of the theoretical product is 0.0127 mol per gram.

TABLE IX

Determination of Acid Soluble Portion of Product of

Attempt to Prepare Dimethyl Lithium Amide

Samples of preparation No 9 in Table VII on page 96 were washed with 250 ml of 1:1 hydrochloric acid and dried in an oven at 260 °C for four hours.

| | Test | | | |
|-----------------------------|----------------|----------------|----------------|----------------|
| | 1 | 2 | 3 | 4 |
| Weight crucible and sample | 15.1512 | 15.4405 | 15.9161 | 15.2374 |
| Weight crucible | <u>14.8917</u> | <u>15.1126</u> | <u>15.8157</u> | <u>15.0261</u> |
| Weight sample | 0.2595 | 0.3279 | 0.1004 | 0.2113 |
| Weight crucible and residue | 14.8980 | 15.1183 | 15.8172 | 15.0289 |
| Weight crucible | <u>14.8917</u> | <u>15.1126</u> | <u>15.8157</u> | <u>15.0261</u> |
| Weight residue | 0.0063 | 0.0057 | 0.0015 | 0.0028 |
| Acid soluble content | 97.57 | 98.26 | 98.51 | 98.67 |
| | % | | | |

TABLE X

Preparation of Naphthyl Alkali-metal Compounds

| | | Preparation | | |
|--|-----|--------------------|--------------------|-----------------------|
| | | <u>1</u> | <u>2</u> | <u>3</u> |
| Alkali-metal | | Na | Na | Li |
| Weight of Alkali-metal | gm | 4.0 | 23.0 | 1.75 |
| Moles of Alkali-metal | mol | 0.174 | 1.0 | 0.254 |
| Weight of Naphthalene | gm | 10.0 | 12.8 | 64.1 |
| Moles of Naphthalene | mol | 0.128 | 0.1 | 0.5 |
| Molar Ratio Alkali-metal to Naphthalene | | 1.36 | 10.0 | 0.508 |
| Theoretical Molar Ratio | | 2.0 | 2.0 | 2.0 |
| Solvent | | ether ^a | ether ^a | ether ^b |
| Volume of Solvent | ml | 50 | 50 | 500 |
| Molar Equivalents Solvent | | 0.483 | 0.483 | 4.83 |
| Atmosphere | | ether | ether | nitrogen ^c |
| Temperature | °C | 25 | 25 | 25 |
| Time of Reaction | hr | 24 | 39 | 5 |
| Product | | NaOH | NaOH | Li ₃ N |
| Amount of Product | mol | trace | trace | 0.23 ^d |

^a^b Ether was taken from container labeled, dry ether.^c Ether was dried with NaH and distilled prior to use.^d Nitrogen was oil pumped.^d Lithium nitride was hydrolyzed with distilled water and analyzed for ammonia and lithium hydroxide, similar to the analysis for amine content.

TABLE XI

Preparation of n-Butyllithium

| | Preparation | | | | |
|----------------------------|----------------------|----------------------|----------|----------|-------------------|
| | <u>1^a</u> | <u>2^b</u> | <u>3</u> | <u>4</u> | |
| Time of Addition of Halide | min | 120 | 35 | 60 | 35 |
| Temperature of Addition | °C | -5 | -10 | 10 | 15 |
| Type of Lithium | | cut ^c | cut | cut | wire ^d |
| Lithium | gm atom | 1.25 ^e | 1.25 | 1.25 | 1.70 |
| Halide | | Br | Br | Cl | Cl |
| Amount of Halide | mol | 0.5 | 0.5 | 0.5 | 0.75 |
| Yield ^f | % | | | 95.5 | 89.7 |
| Stirring after Addition | hr | 5 | 1 | 1 | 0.75 |
| Stirring Temperature | °C | -10 | -10 | 15 | 20 |

^a During the preparation, due to a vacuum generated in the reaction vessel, the mercury in the mercury-seal stirrer was drawn into the reaction vessel, and combined with the unreacted lithium to form an amalgam. Since the conditions were so altered, yield was not determined.

^b The reaction mixture was filtered with a sintered glass filter. The porosity of the filter was so fine that four hours were required to filter 300 milliliters of solution, and due to the excessive length of filtration the solvent part of the filtrate evaporated and some of the n-butyllithium decomposed. Therefore, yield was not determined.

^c The lithium was scraped clean of oxide, hammered into a thin sheet, cut into ribbons, and then cut into small pieces measuring 1x5x3 millimeters.

^d The lithium wire was weighed, washed with dry ether, and cut into five millimeter length before addition to the reaction.

^e An excess of 0.2 mol of lithium was added to the reaction in case of any reaction of the lithium with the nitrogen atmosphere.

^f Since all the preparations were carried out in petroleum ether, in which lithium halides are insoluble, the yields were determined after filtration, by titration with standard hydrochloric acid to the phenolphthalein end point.

Preparation of Dimethyl Lithium Amide. Dimethyl amine was passed through the n-butyllithium mentioned in the above paragraph, and the products from the four preparations were analyzed for dimethyl lithium amide. The data from the analyses of the products are listed in Table XII on page 102.

The solubility of the prepared dimethyl lithium amide in dimethyl amine and ammonia was determined by measuring the conductivity of the solutions. The data obtained are listed in Table XIII on page 103.

Electrolysis of Dimethyl Lithium Amide in Liquid Ammonia. The data obtained during the electrolysis of dimethyl lithium amide and the analysis of the product of the electrolysis are listed in Table XIV on page 104.

The data observed during the electrometric titration of the electrolysis product are listed in Table XV on page 105. The curve constructed from the data is shown in Figure 16 on page 106.

The data observed during the determination of the molecular weight of the electrolysis product by the depression of the freezing point of benzene are listed in Table XVI on page 107. The curve constructed from the data is shown in Figure 17 on page 108.

TABLE XII

Analysis of Product of Attempts to Prepare
Dimethyl Lithium Amide from Butyllithium
and Dimethyl Amine

| | | Preparation | | | |
|--|-----|----------------------|----------------------|----------------------|----------------------|
| | | <u>1^a</u> | <u>2^b</u> | <u>3^c</u> | <u>4^c</u> |
| <u>Receiver:</u> | | | | | |
| Volume of Hydrochloric Acid ^d | ml | 35.00 | 35.00 | 35.00 | 35.00 |
| Milliequivalents | | 35.20 | 35.20 | 35.20 | 35.20 |
| Volume of Sodium Hydroxide ^e | ml | 35.25 | 34.80 | 22.55 | 26.10 |
| Milliequivalents | | 34.60 | 34.30 | 22.18 | 25.65 |
| Amine | mol | 0.6 | 0.9 | 13.02 | 9.55 |
| <u>Still:</u> | | | | | |
| Volume of Sodium Hydroxide ^e | ml | 25.80 | 25.86 | 25.26 | 25.46 |
| Milliequivalents | | 25.40 | 25.40 | 24.85 | 25.05 |
| Volume of Hydrochloric Acid ^d | ml | 26.00 | 26.91 | 38.59 | 34.55 |
| Milliequivalents | | 26.15 | 27.01 | 38.80 | 34.70 |
| Lithium | mol | 0.75 | 1.61 | 13.95 | 9.65 |
| <u>Yield, Based on Lithium:</u> | | | | | |
| Dimethyl Lithium Amide | % | 80.0 | 55.8 | 93.4 | 98.9 |

^a A sample dried in a nitrogen atmosphere was analyzed.

^b A sample dried in a nitrogen atmosphere was analyzed after 11 hours storage under nitrogen.

^c A sample in a petroleum ether suspension was analyzed immediately after formation

^d The hydrochloric acid solution was 1.00% normal.

^e The sodium hydroxide solution was 0.98% normal.

TABLE XIII

Determination of Conductivity of Dimethyl Lithium Amide
in Dimethyl Amine and Ammonia

| | R_1^a ohms | R_2^b ohms | R_c^c ohms | K^d | J^e |
|--|-----------------|-----------------|-----------------|-------|-----------------------|
| <u>Standardization of Conductivity Cell:</u> | | | | | |
| 0.1 N Potassium chloride ^f | 190 | 543 | 225.5 | 2.903 | |
| <u>Determination of Conductivity:</u> | | | | | |
| Dimethyl Lithium Amide in Dimethyl Amine | 100,000 | 938 | 1,513,000 | 2.903 | 1.92×10^{-6} |
| Dimethyl Lithium Amide in Ammonia | 8,200 | 370 | 4,820 | 2.903 | 6.03×10^{-4} |

a Decade resistance box reading.
 b Slide wire resistance reading.
 c Conductivity cell resistance, calculated.
 d Cell constant.
 e Conductivity.
 f The specific conductance of 0.1 N potassium chloride is 0.01289.

TABLE XIV

Electrolysis of Dimethyl Lithium Amide
in Liquid Ammonia

| | | Preparation | | |
|-----------------------------------|----------|--------------------|----------------------|--------------------|
| | | <u>1</u> | <u>2^a</u> | <u>3</u> |
| <u>Electrolysis:</u> | | | | |
| Dimethyl Lithium Amide | No | 3 | 3 | 4 |
| | gm | 5 | 3 | 3 |
| Ammonia | ml | 600 | 520 | 570 |
| Temperature | °C | -33 | -33 | -33 |
| Quantity of Electricity | coulombs | 8412.5 | 4287 | 7726 |
| Time of Electrolysis | hr | 6 | 2 | 12 |
| Quantity of Product | ml | 2.5 | --- | 1.5 |
| <u>Analysis of Product:</u> | | | | |
| B.p. 715 from Ether | °C | 74 | | 74 |
| B.p. 715 from Benzene | °C | 75 | | .. |
| Specific Gravity _{25 °C} | | 0.774 | | 0.778 |
| Equivalent Weight ^b | | 254 | | ... |
| Molecular Weight ^c | | 257 | | ... |
| Per Cent Carbon | % | ^d | | 15.28 ^e |
| Per Cent Hydrogen | % | | | 10.10 |
| Per Cent Nitrogen | % | | | 12.05 |
| Per Cent Oxygen ^f | % | | | 62.57 |
| Per Cent Chloride | % | 0.00 | | 0.00 |
| Per Cent Lithium | % | 0.00 | | 0.00 |

^a Apparatus connections ruptured after two hours due to excess internal pressure caused by evaporating ammonia.

^b From electrometric titration with standard hydrochloric acid.

^c From depression of the freezing point of benzene.

^d Insufficient sample remained for elemental analysis.

^e Elemental analysis by Micro-Tech Laboratories, Skokie, Ill.

^f Per cent oxygen was calculated by difference.

TABLE XV

Electrometric Titration of Product of Electrolysis
of Dimethyl Lithium Amide

| Weight of Sample | | gm | 0.1302 | |
|-------------------------------------|-----------------------|-------------------------|-----------|--|
| Volume of water added | | ml | 25.0 | |
| <u>HCl^a</u> <u>ml</u> | <u>pH^b</u> | <u>HCl</u> <u>ml</u> | <u>pH</u> | |
| 0.0 | 9.80 | 90.0 | 6.65 | |
| 1.0 | 9.70 | 95.0 | 6.55 | |
| 2.0 | 9.68 | 100.0 | 6.40 | |
| 3.0 | 9.55 | 105.0 | 6.18 | |
| 4.0 | 9.50 | 110.0 | 6.03 | |
| 8.0 | 9.45 | 115.0 | 5.90 | |
| 12.0 | 9.35 | 120.0 | 5.80 | |
| 16.0 | 9.27 | 125.0 | 5.70 | |
| 20.0 | 9.18 | 130.0 | 5.60 | |
| 24.0 | 9.05 | 135.0 | 5.50 | |
| 28.0 | 9.00 | 140.0 | 5.30 | |
| 32.0 | 8.87 | 145.0 | 5.15 | |
| 36.0 | 8.71 | 145.0 ^c | 6.00 | |
| 40.0 | 8.52 | 150.0 | 5.90 | |
| 43.0 | 8.35 | 155.0 | 5.80 | |
| 45.0 | 8.25 | 160.0 | 5.70 | |
| 48.0 | 8.10 | 165.0 | 5.55 | |
| 50.0 | 8.00 | 170.0 | 5.45 | |
| 56.0 | 7.70 | 175.0 | 5.25 | |
| 60.0 | 7.52 | 180.0 | 5.05 | |
| 65.0 | 7.32 | 185.0 | 4.95 | |
| 70.0 | 7.15 | 190.0 | 4.73 | |
| 75.0 | 7.00 | 195.0 | 4.60 | |
| 80.0 | 6.85 | 200.0 | 4.45 | |
| 85.0 | 6.80 | 205.0 | 4.30 | |

^a The hydrochloric acid was 0.0029 normal.

^b The pH of the water in which the sample was dissolved was 5.25.

^c pH Meter restandardized.

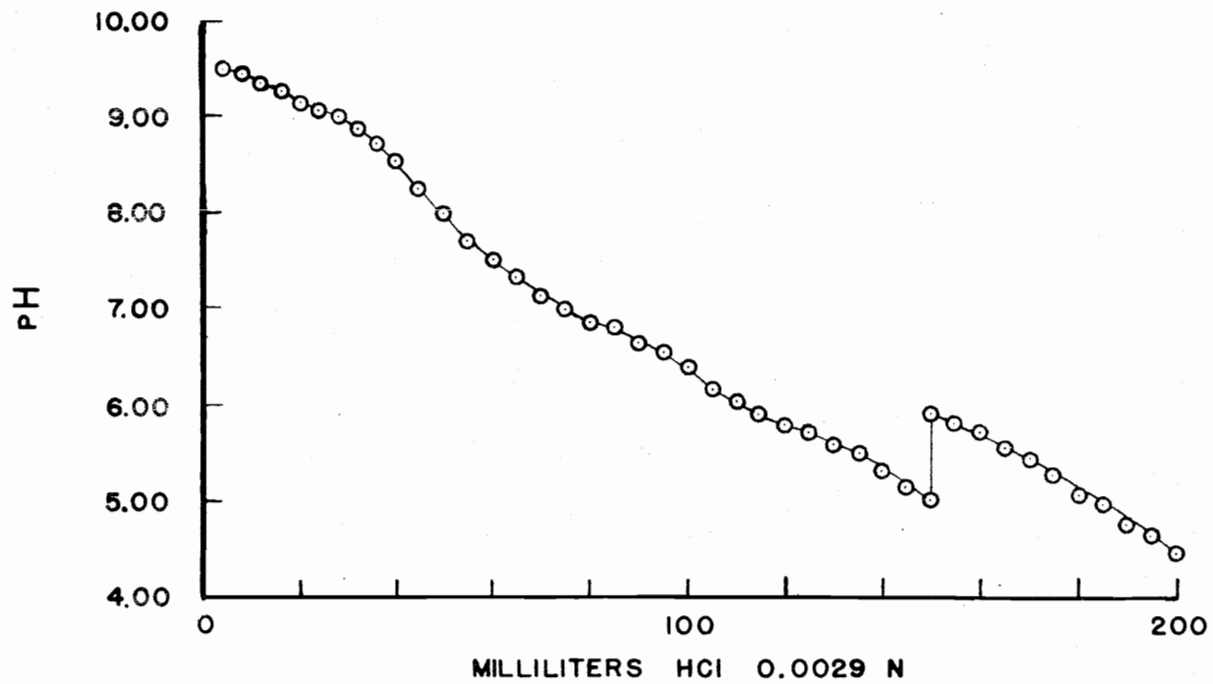


FIGURE 16. ELECTROMETRIC TITRATION OF ELECTROLYSIS PRODUCT

TABLE XVI

Freezing Point Depression of Benzene
by Electrolysis Product

| <u>Freezing Point of Benzene^a</u> | | <u>Depressed Freezing Point^b</u> | |
|--|--|---|--|
| <u>Time</u> <u>min</u> | <u>Temp</u> <u>- °B^c</u> | <u>Time</u> <u>min</u> | <u>Temp</u> <u>- °B^c</u> |
| 9.5 | 2.760 | 0.0 | 2.470 |
| 10.0 | 2.730 | 0.5 | 2.410 |
| 11.0 | 2.690 | 1.0 | 2.360 |
| 12.0 | 2.650 | 2.0 | 2.340 |
| 13.0 | 2.630 | 4.0 | 2.330 |
| 15.0 | 2.620 | 6.0 | 2.320 |
| 17.0 | 2.600 | 8.0 | 2.310 |
| 19.0 | 2.620 | 10.0 | 2.305 |
| 19.5 | 2.630 | 12.0 | 2.300 |
| 20.0 | 2.640 | 13.0 | 2.295 |
| 20.5 | 2.640 | 14.0 | 2.290 |
| 21.0 | 2.640 | 15.0 | 2.285 |
| 21.5 | 2.640 | 16.0 | 2.280 |
| 22.0 | 2.650 | 16.5 | 2.280 |
| 22.5 | 2.640 | 17.0 | 2.280 |
| 23.0 | 2.650 | 17.5 | 2.280 |
| 23.5 | 2.650 | 18.0 | 2.280 |
| 24.0 | 2.650 | 18.5 | 2.280 |
| 24.5 | 2.650 | 19.0 | 2.280 |
| 25.0 | 2.650 | 19.5 | 2.275 |
| 25.5 | 2.650 | 20.0 | 2.275 |
| 26.0 | 2.650 | 20.5 | 2.265 |
| 27.0 | 2.650 | 21.0 | 2.265 |
| 28.0 | 2.650 | 22.0 | 2.255 |
| 28.5 | 2.650 | 23.0 | 2.250 |
| 29.0 | 2.650 | 24.0 | 2.250 |
| 29.5 | 2.650 | 25.0 | 2.245 |
| 30.0 | 2.650 | 26.0 | 2.240 |
| 30.5 | 2.650 | 27.0 | 2.230 |
| 31.0 | 2.650 | 29.0 | 2.220 |
| 31.5 | 2.650 | 31.0 | 2.170 |
| 32.0 | 2.610 | 33.0 | 2.150 |
| 33.0 | 2.550 | 35.0 | 2.100 |
| 34.0 | 2.520 | 37.0 | 2.065 |
| 35.0 | 2.500 | 39.0 | |

^a Sample of 12.91 gm Benzene was used.

^b To the 12.91 gm of Benzene 0.24 gm of product of the electrolysis of dimethyl lithium amide was added.

^c Degrees below zero on the Beckman freezing point thermometer.

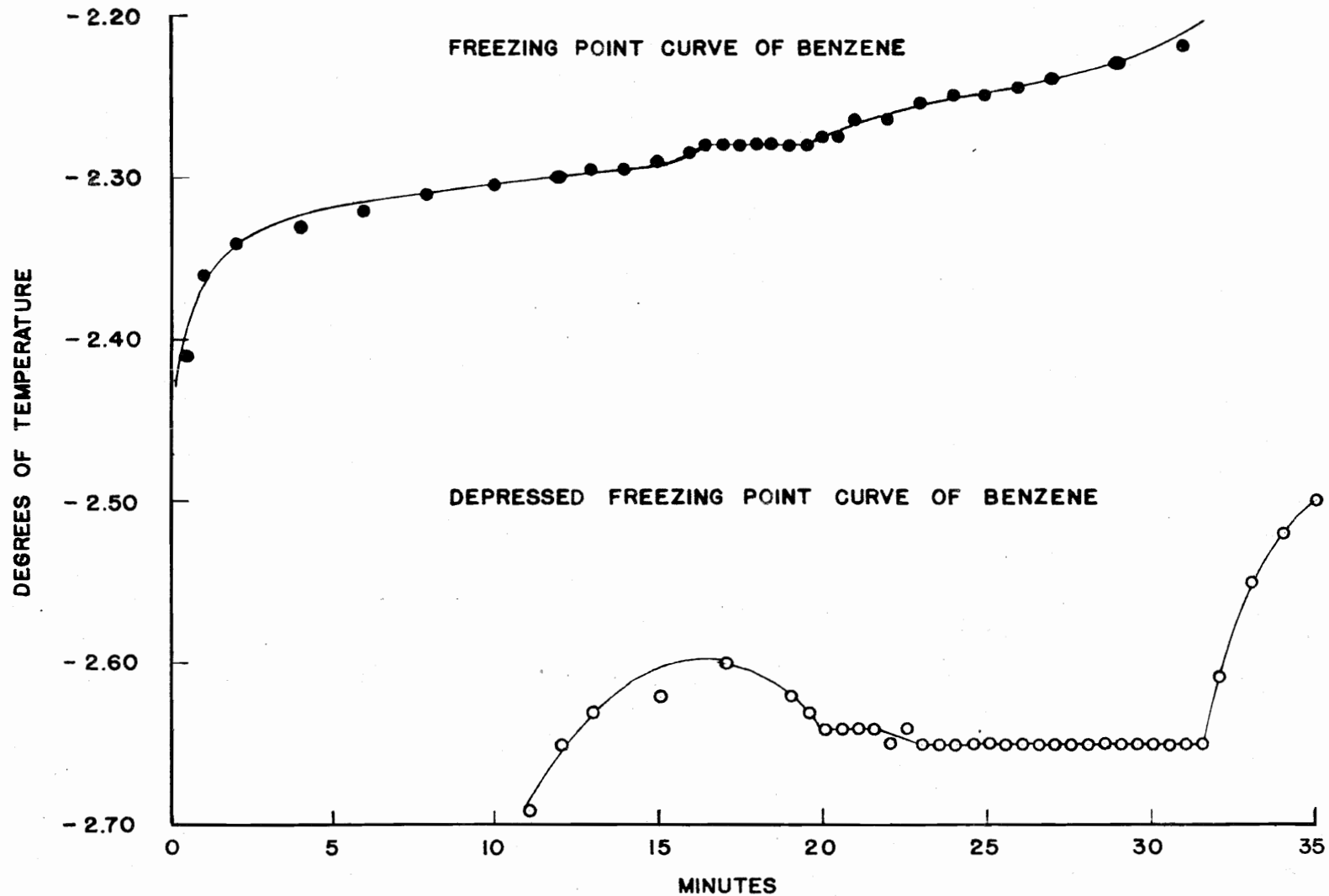


FIGURE 17. FREEZING POINT DEPRESSION OF BENZENE BY ELECTROLYSIS PRODUCT

Sample Calculations

An example of each calculation made in the course of this investigation is described in the following paragraphs.

Conductivity of Dimethyl Lithium Amide Solutions. To determine the conductivity of dimethyl lithium amide solutions, the conductivity cell constant, K , had to be determined.

The resistance of the conductivity cell was measured in 0.1 normal potassium chloride with a bridge circuit. The resistance was calculated by dividing the product of resistance one and resistance two by 1000 minus resistance two as follows: Data was taken from Table XIII on page 103.

$$R_c = \frac{R_1 R_2}{1000 - R_2}$$

where:

R_c = Resistance of cell in 0.1 N potassium chloride, ohms

R_1 = Decade resistance box setting, ohms

R_2 = Slide wire resistance setting, ohms

$$R_c = \frac{190 \times 543}{1000 - 543}$$

$$R_c = 225.5$$

The conductivity cell constant, K , was calculated by multiplying the resistance of the cell in 0.1 normal potassium chloride

by the specific conductance of 0.1 normal potassium chloride, 0.01289 mho as follows:

$$K = R_c \times 0.01289$$

where:

K = Conductivity cell constant

R_c = Resistance of cell in 0.1 N potassium chloride, ohms

$$K = 225.5 \times 0.01289$$

$$K = 2.903$$

The conductivity of the dimethyl lithium amide solution was calculated by dividing the cell constant, K , by the resistance of the cell in the dimethyl lithium amide solution as follows:

$$J = \frac{K}{R_c}$$

where:

J = Conductivity of the dimethyl lithium amide solution, mho

K = Conductivity cell constant

R_c = Cell resistance in dimethyl lithium amide solution, ohms

$$J = \frac{2.903}{1,513,000}$$

$$J = 1.92 \times 10^{-6}$$

Determination of Yield of n-Butyllithium. After lithium halide had been removed by filtration, an aliquot of the n-butyl-

lithium solution was titrated with standard hydrochloric acid. The yield was calculated using the following equation: The data was taken from Table XI on page 100.

$$Y = \frac{V \times N \times v \times M \times 100}{1000 \times A \times W}$$

where:

- Y = Yield of n-butyllithium, %
- V = Volume of acid used in titration, ml
- N = Normality of acid used in titration
- v = Volume of n-butyllithium solution, ml
- A = Volume of aliquot, ml
- W = Weight of organic halide used, gm
- M = Molecular weight of organic halide, gm

$$Y = \frac{12.47 \times 0.995 \times 325 \times 92.6 \times 100}{1000 \times 6 \times 69.5}$$

$$Y = 89.7$$

Determination of Amine Content. The amine was liberated from the sample and absorbed in hydrochloric acid which was titrated with standard sodium hydroxide. The amine content was calculated from the following equation: A sample of preparation one in Table VII on page 96 was used.

$$A = \frac{(V_1 \times N_1 - V_2 \times N_2) M \times 100}{1000 \times S}$$

where:

- A = Amine content, %
- V₁ = Volume of acid in receiver, ml
- N₁ = Normality of acid in receiver
- V₂ = Volume of base used in titration, ml
- N₂ = Normality of base used in titration
- M = Molecular weight of amine
- S = Weight of sample, gm

$$A = \frac{(80 \times 0.501 - 23.10 \times 0.493) 129 \times 100}{1000 \times 5.00}$$

$$A = 79.3$$

Determination of Dimethyl Lithium Amide. The yield of amide was calculated from data obtained in the analysis for amine content, as follows: The data were taken from the analysis of preparation three as listed in Table XII on page 102.

$$Y = \frac{(V_1 \times N_1 - V_2 \times N_2) \times 100}{(V_3 \times N_3 - V_4 \times N_4)}$$

where:

- Y = Yield of dimethyl lithium amide, %
- V₁ = Volume of acid added to receiver, ml
- N₁ = Normality of acid added to receiver
- V₂ = Volume of base used to titrate receiver contents, ml
- N₂ = Normality of base used in titration
- V₃ = Volume of acid used to titrate still contents, ml
- N₃ = Normality of acid used in titration

V_b = Volume of base added to still, ml

N_b = Normality of base added to still

$$Y = \frac{(35 \times 1.004 - 22.55 \times 0.984) \times 100}{(38.59 \times 1.004 - 25.26 \times 0.984)}$$

$$Y = 93.5$$

Determination of Alkali-metal Content. The alkali-metal in the unknown sample was converted to the sulfate, and all other material was distilled off. The alkali-metal content of a sample from preparation five in Table VII on page 96 was calculated by the following equation:

$$M = \frac{R \times 2A \times 100}{S \times W}$$

where:

M = Alkali-metal content, %

R = Weight of sulfate residue, gm

A = Molecular weight of alkali-metal, gm

W = Molecular weight of alkali-metal sulfate, gm

S = Weight of sample, gm

$$M = \frac{0.5467 \times 2(7) \times 100}{0.4984}$$

$$M = 13.91$$

Determination of Specific Gravity. The specific gravity was calculated with the following equation, by dividing the weight of water in the pycnometer into the weight of sample contained by the

pycnometer. A sample of preparation one in Table XIV on page was used.

$$S = \frac{P}{W}$$

where:

S = Specific gravity of the sample

P = Weight of sample contained by the pycnometer, gm

W = Weight of water contained by the pycnometer, gm

$$S = \frac{0.3870}{0.5001}$$

$$S = 0.774$$

Determination of Acid Soluble Portion. The acid soluble content of the sample was calculated by dividing the weight of residue by the weight of sample, subtracting from one, and multiplying the result by 100. The data was taken from Test one in Table IX on page 98.

$$A = (1 - \frac{R}{S})100$$

where:

A = Acid soluble content of sample, %

R = Weight of residue, gm

S = Weight of sample, gm

$$A = 1 - \left[\frac{0.0063}{0.2595} \right] 100$$

$$A = 97.57$$

Determination of Water Insoluble Gas Evolved. The volume of gas evolved by the sample was corrected to standard temperature and pressure, and with it the water insoluble gas content of the sample was calculated. The data was taken from test two in Table VII on page 77.

$$G = \frac{V \times T_s \times (P - p)}{100 T \times P_s \times L \times W}$$

where:

G = Water insoluble gas content, mol/gm

V = Volume of gas evolved from sample, ml

T = Temperature of gas, °K

P = Atmospheric pressure, mm of mercury

p = Partial pressure of water, mm of mercury

W = Weight of sample, gm

L = Liters per mol of gas at standard conditions

T_s = Standard temperature, °K

P_s = Standard pressure, mm of mercury

$$G = \frac{4.6 \times 273 \times (711.3 - 24.5)}{100 \times 298.5 \times 760 \times 22.4 \times 0.1237}$$

$$G = 13.7 \times 10^{-3}$$

Determination of Equivalent Weight by Electrometric Titration.

The equivalent weight was calculated by the following equation from the weight of sample and the volume and normality of the acid used to titrate the sample to the pH of the diluting water after restandardization of the pH meter.

$$E = \frac{S \times 1000}{V \times N}$$

where:

E = Equivalent weight of the sample

S = Weight of sample, gm

V = Volume of acid used in titration, ml

N = Normality of acid

$$E = \frac{0.1302 \times 1000}{177 \times 0.0029}$$

$$E = 254$$

Determination of Molecular Weight by Depression of the Freezing

Point of Benzene. The molecular weight was calculated by the following equation.

$$M = \frac{1000K_f g}{G T_f}$$

where:

K_f = Constant for benzene

g = Weight of sample, gm

G = Weight of solvent, benzene, gm

T_f = Lowering of freezing point, °C

M = Molecular weight of sample, gm

$$M = \frac{1000 \times 5.12 \times 0.24}{12.91(2.65 - 2.28)}$$

$$M = 257$$

IV. DISCUSSION

This section contains a discussion of the results obtained during the course of this investigation, recommendations for future work, and the limitations observed during the experimental work.

Discussion of Results

A discussion of the results obtained is presented in the following paragraphs.

Preparation of Di-n-butyl Sodium Amide. This preparation was attempted to gain familiarity with the method invented by Ziegler^(74, 75,76,77). Sodium and di-n-butyl amine were chosen as reagents since they are both simpler to prepare and handle than lithium and dimethyl amine for example. The data may be found as run one in Table VII on page 96.

Cut sodium was reacted with di-n-butyl amine in the presence of naphthalene, dissolved in ether, in a nitrogen atmosphere with stirring. An excess of sodium was used to allow for any side reactions with air and water.

The white insoluble product formed was separated from the reaction mixture by filtration and analyzed. The analysis showed 73.9 per cent di-n-butyl amine and 18.9 per cent sodium. The difference of 7.2 per cent was largely naphthalene. Only 13.2 per cent

sodium could have been attached to the amine in the amide form. The rest was present as the hydroxide. Since the nitrogen was water pumped and passed through a water bubbler, the atmosphere in the reaction flask must have been saturated with water, which would account for the formation of sodium hydroxide. The filtration of the product was carried out in the air, and it was determined later that ether removed from its original container contained as much as 30 per cent water.

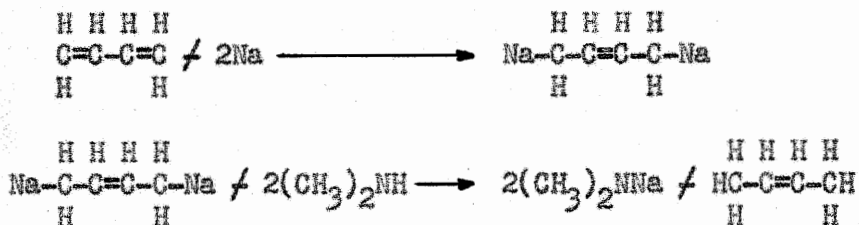
Preparation of Dimethyl Sodium Amide. This section contains a discussion of test two, three, four, and five in Table VII on page 96. Cut sodium was reacted with dimethyl amine in the presence of 1,3 butadiene until all the sodium metal was dissolved. Butadiene 1,3 was used instead of naphthalene, because removal from the product would involve a simple distillation at room temperature, and the 1,3 butadiene condenses at a temperature only 10 °C lower than dimethyl amine. The use of nitrogen was considered unnecessary since the refluxing amine and 1,3 butadiene would provide a compatible atmosphere.

The product was filtered and analyzed. The analysis showed 58.8 per cent amine and 30.5 per cent sodium, as compared with 65.70 per cent amine and 34.30 per cent sodium in dimethyl sodium amide. The remaining 10.4 per cent could not be identified. The product decomposed at 109 - 114.5 °C. One-half of the product was contaminated by the filter, and the rest was not enough for any additional analysis or electrolysis.

Since the previous reaction required 19 hours to attain completion, it was assumed that with highly dispersed sodium the reaction velocity could be increased. Therefore, a highly dispersed sodium suspension was used in the next preparation. Dispersed sodium, suspended in toluene, was reacted with dimethyl amine in the presence of 1,3 butadiene in a nitrogen atmosphere at -3°C for 14 hours. The sodium beads remained, but the dimethyl amine, 1,3 butadiene, and toluene had reacted to form a black tar like mass which could not be separated. The reaction mixture was discarded.

An attempt was made to prepare one mol of dimethyl sodium amide, so that a sufficient quantity of the amide would be available for analysis.

Cut sodium was reacted with dimethyl amine in the presence of 1,3 butadiene. The apparatus had been thoroughly flushed with nitrogen before addition of the reagents. Butadiene was condensed on upon the sodium for one-half hour. The sodium changed color from silver to dark gray, which indicated reaction between the sodium and 1,3 butadiene. The postulated product was a sodium addition compound of 1,3 butadiene with rearrangement of the double bonds. Then, dimethyl amine was condensed into the reaction flask. Upon addition of the dimethyl amine, small bubbles emanated from the surface of the sodium lumps. After ten minutes the sodium regained its silvery color. The amine must have reacted with the coating on the sodium lumps with the liberation of hydrogen. The postulated equation⁽⁷⁷⁾ is as follows:



Upon further addition of dimethyl amine a white crust formed on the sodium lumps which was assumed to be dimethyl sodium amide. After dimethyl amine had been added for 55 minutes, the reaction mixture became yellow-green. Butadiene 1,3 was added for an additional 30 minutes, and the mixture was refluxed for 15 minutes, with a subsequent addition of dimethyl amine for 10 minutes. A vacuum of 3.5 inches of mercury occurred in the apparatus and mercury from the mercury-seal stirrer was drawn into the reaction flask. It was not expected that this mercury would influence the reaction unfavorably, since for early preparation methods, organo-metallic compounds were made using a mercury-alkali-metal alloy⁽⁵⁸⁾. The pressure was increased by the addition of nitrogen. After one hour the mixture became cloudy and deep yellow in color which changed to dark brown.

After settling and refluxing for seven hours the mixture had changed to bright silvery, unreacted sodium lumps suspended in a light yellow gel. Some bubbling was observed, which was excess dimethyl amine boiling off.

The previous experiment was repeated, but naphthalene was substituted for 1,3 butadiene as shown in run five in Table VII on page 96.

Cut sodium was reacted with dimethyl amine in the presence of naphthalene dissolved in freshly distilled ether, at 7 °C with stirring.

An unsuccessful attempt was made to weigh the dimethyl amine used, by condensing it into a preweighed flask, weighing and recondensing into the reaction flask.

Upon addition of dimethyl amine to the sodium and dissolved naphthalene, an orange color, indicative of naphthylalkali-metal compounds, was observed. After 45 minutes a white precipitate appeared, which was assumed to be dimethyl sodium amide. After an additional two hours, the reaction mixture acquired a deep red color, indicating the formation of naphthylsodium. Amine was added for 40 more minutes, and after five hours, a white cake of amide had settled to the bottom of the reaction flask. The mixture was stirred and became golden brown indicating that some naphthylsodium remained. Dimethyl amine was added for another 15 minutes, and wherever the drops of amine hit the mixture a white color resulted. When the thimble condenser was removed from the apparatus, two drops of water fell into the reaction mixture, which turned white immediately. The water reacted with any remaining naphthylsodium preferentially, removing any color.

The reaction mixture was heated to 160 °C for four hours and 180 °C for one hour under vacuum, to remove ether, naphthalene and dihydronaphthalene. The solid residue was washed with dried ether and dried under nitrogen. Since an analysis of the product showed 3.0 per cent amine and 0.96 per cent nitrogen, it was assumed that

during the separation by distillation at such high temperatures any amide present in the product was destroyed. Product from a similar preparation decomposed at a temperature 109 - 114.5 °C at atmospheric pressure.

Preparation of Dimethyl Lithium Amide. The preparation of dimethyl lithium amide was attempted after that of di-n-butyl sodium amide. Due to the difficulties in preparing the lithium metal for reaction, sodium was then substituted in the later preparations.

Cut lithium was reacted with dimethyl amine in the presence of 1,3 butadiene until all the lithium had dissolved. Dimethyl amine was condensed upon the lithium flakes for five minutes, but no evidence of reaction was observed. Therefore, 1,3 butadiene was added and immediately vigorous bubbling occurred at the surface of the lithium. Ten minutes after the beginning of the reaction the mixture became cloudy and light yellow-green in color. Amine and butadiene were added alternately until all the lithium had dissolved. The reaction mixture became yellow which was due to the reacted butadiene. The precipitate was filtered out, but was not enough for analysis.

An attempt was made (run no 7, Table VII on page 96) to prepare dimethyl lithium amide as before except that naphthalene was substituted for 1,3 butadiene.

Cut lithium was reacted with dimethyl amine in the presence of naphthalene dissolved in dried, freshly distilled ether at 7 °C for six hours with stirring. A light precipitate observed at the beginning of the reaction was lithium oxide. After 30 minutes of amine addition

the lithium became bright and then gold in color indicative of naphthyllithium. A white precipitate was formed which was assumed to be dimethyl lithium amide. The reaction mixture became yellow. The precipitate was removed by filtration and washed with dried ether on a sintered glass filter in a dry box. The analysis showed 9.3 per cent amine and 2.90 per cent nitrogen. These low figures could only be explained by the fact that the reaction did not occur as assumed, or that exposure of the product during handling had caused decomposition of any amide.

Preparation of Diethyl Lithium Amide. Since all previous preparations by the Ziegler method⁽⁷⁷⁾ either gave no results or at the best very poor and irregular results, an exact duplication of the first example in the patent⁽⁷⁷⁾ was attempted. This was run 8, Table VII, page 96.

Cut lithium was reacted with diethyl amine, in the presence of naphthalene dissolved in ether in a nitrogen atmosphere. Since the patent was not clear in regard to refluxing, the mixture was permitted to react with stirring at 25 °C, for 41 hours. No reaction occurred. The reaction flask was then heated with a water bath so that gentle refluxing took place. After two hours the mixture became orange in color, and after 10.0 hours all the lithium had dissolved. A precipitate had been formed, and the entire mixture had become dark brown. The precipitate was filtered and washed with benzene. The product did not react with water as an amide would have. All these observations are in direct contradiction to the patent.

The previously described preparation of diethyl lithium amide was repeated exactly, run 9, Table VII, page 96, but the reaction mixture was refluxed from the beginning. After five minutes, frothing occurred around the lithium and the metal acquired a golden color. A yellow precipitate was formed in the vicinity of the lithium. The precipitate became white and in 30 minutes, yellow again. After another hour all the lithium had gone into solution. The reaction mixture then became brown and the reaction was stopped after 2.5 hours.

The entire mixture was dissolved in benzene. The ether, benzene, naphthalene and any dihydronaphthalene were distilled off under vacuum. The solid residue was analyzed. Amine content varied from 0 to 58 per cent indicating a nonuniform substance. The lithium content was 20.15 per cent and an elemental analysis showed only 1.60 per cent nitrogen. If an amide had been formed during the reaction most of it had been destroyed when the precipitate was separated by distillation under vacuum.

Various tests were made with the product. Upon drying at 144 °C for 11.5 hours the material lost weight. This could be caused by the destruction of any remaining amide. After further drying at 134 °C for 23.5 hours the material gained weight. This result could be caused by reaction with oxygen and carbon dioxide or the hydrolysis of any lithium nitride present.

In a determination of gas evolved, all but one value were greater than that for the theoretical product. This result could point to the presence of lithium nitride. The results were confirmed by a determi-

nation of the acid soluble portion of the material. This also indicated the presence of some carbonaceous material.

Preparation of Diethyl Sodium Amide. An attempt (run no 10, Table VII on page 96) was made to electrolyze diethyl amine between a sodium anode and a chromel cathode to form dimethyl lithium amide. The amine did not pass any current at 95 volts, and the experiment was discarded.

Preparation of Naphthyl Alkali-metal Compounds. An attempt was made to prepare naphthylsodium and naphthyllithium in order to investigate the first step of the Ziegler reaction⁽⁷⁷⁾. The data is presented in Table X on page 99.

Cut sodium was reacted with naphthalene, dissolved in ether, at 25 °C. A gold color was observed on the sodium lumps which indicated the formation of some naphthylsodium. After 24 hours the lumps of sodium were covered with a white crust which consisted of sodium hydroxide. Water in the ether had reacted with some of the sodium to form the crust. The reaction was repeated and again after 39 hours a crust of sodium hydroxide had formed.

Cut lithium was reacted with naphthalene, dissolved in dried ether, in a nitrogen atmosphere, at 25 °C. After five hours a brown precipitate had formed. The precipitate was separated by filtration. It reacted very slowly with water as compared with other organoalkali compounds. On hydrolysis an ammonia like gas was evolved, this indicated that the brown precipitate was lithium nitride.

Preparation of n-Butyllithium. Due to an inability to prepare the disubstituted alkali-metal amides according to the Ziegler method⁽⁷⁷⁾, the method improved by Gilman and co-workers⁽²¹⁾ was substituted.

n-Butyllithium was chosen because it can be prepared in yields of 90 per cent. The yield also is not affected by the size of the lithium particles and the rate of addition of the halide.

Two attempts to prepare n-butyllithium were made. With the stirrer started, 30 drops of a solution of n-butyl bromide in dried, freshly distilled ether were added to cut lithium in dried, freshly distilled ether. The reaction mixture was cooled to -10°C with a dry ice - methyl alcohol bath. After the reaction had started the remainder of the n-butyl bromide solution was added at an even rate over 30 minutes. In each preparation the rate of reaction became too rapid, and mercury from the stirrer was sucked into the reaction flask. Both the preparations were used to gain experience in this type of preparation.

The preparation was repeated twice in the same manner successfully with n-butyl bromide and cut lithium in petroleum ether. Petroleum ether was substituted for diethyl ether because its use has several advantages. The difficulty of secondary reactions like cleavage of diethyl ether is removed. Indirect supplementary analyses⁽⁷⁸⁾ are not necessary to determine the titer of solution, and the simple acid titration analysis⁽³³⁾ is sufficient. The by-products, like lithium halide, are insoluble in petroleum ether and may be removed by filtration. Some of these filtered solutions have

have been kept for extended periods with no significant change. The data in Table XI on page 100 show that yields approaching 90 per cent were attained. The preparation was repeated twice more, and n-butyl chloride was substituted for n-butyl bromide. A yield as high as 95 per cent was obtained.

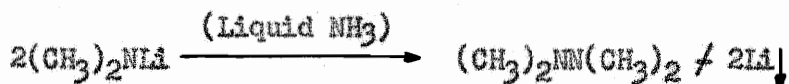
The butyllithium solutions obtained by the test preparations were filtered with a sintered glass filter. The filtration in each case required more than four hours for 250 milliliters of solution, and most of the ether boiled off causing deterioration of the n-butyl-lithium. Therefore, n-butyllithium solutions prepared in the succeeding four tests were filtered through packed glass wool which was proved to be entirely sufficient⁽²⁸⁾.

Preparation of Dimethyl Lithium Amide From Butyllithium. The filtered solutions of n-butyllithium were analyzed for n-butyllithium. Dimethyl amine was passed into the n-butyllithium solutions against a pressure of 40 millimeters of mercury above atmospheric pressure. A white precipitate formed at once. After two hours the precipitate became so thick that 100 milliliters of dried petroleum ether was added to facilitate stirring. After four hours the reaction was completed. The products were analyzed for amine and lithium content in a dry state and in ether suspension. The data in Table XII on page 102 shows that the yield of dimethyl lithium amide based on lithium was as high as 99 per cent when the product was analyzed still in ether suspension. If the product was dried, or stored under nitrogen

even for a short time some of the amide was destroyed and the yield was substantially less.

Solubility and Conductance of Dimethyl Lithium Amide. With an electrolysis of dimethyl lithium amide in mind, dimethyl amine and ammonia were chosen as possible solvents to be tested. Both are similar in structure to dimethyl lithium amide so that secondary reactions were not likely. Also most other solvents were ruled out due to the amides great reactivity, and it was shown in the preparation that the amide would not be sufficiently soluble in hydrocarbons. The determination was made by finding the conductivity of dimethyl lithium amide in dimethyl amine and ammonia with a conductivity cell and a bridge circuit using an oscilloscope instead of earphones. Since the conductivity was much greater in ammonia as shown in Table XIII on page 103, ammonia was chosen as the solvent to be used in the electrolysis.

Electrolysis of Dimethyl Lithium Amide. The electrolysis was carried out between a mercury cathode and a platinum anode. The purpose of the mercury cathode was to take up the liberated lithium in a mercury-lithium amalgam. The postulated equation for the reaction is as follows:



The dimethyl lithium amide in its ether suspension was transferred to the electrolytic cell. There the ether was distilled off under vacuum, and immediately ammonia was condensed upon the amide. The dimethyl lithium amide was stirred into solution with a stirring magnet which

floated on the mercury cathode. The stirring magnet also served to break up any scum that formed on the cathode. After sufficient ammonia had been condensed into the reaction flask to cover the electrodes, the electrolysis was begun. The reaction mixture turned black and the apparatus iced up so that the reaction could not be observed properly. After the theoretical coulombs had passed through the reaction or as in electrolysis two the apparatus was ruptured, the current was turned off. The ammonia layer was decanted from the mercury cathode and permitted to evaporate while shielded against the atmosphere.

The product of the electrolysis was a clear viscous liquid having a fishlike odor. The liquid was soluble in water and slightly soluble in ether and benzene. The specific gravity was determined in a pycnometer as 0.774. The boiling point of the product was clear and exact at 74 °C. An electrometric titration of a sample of the product showed that it was a very weak base. A pH curve was plotted from the titration data but no inflection point was observed. Since there was no inflection point, the pH of the water in which the sample had been dissolved was taken as the arbitrary inflection point to calculate the equivalent weight, which was 254. A molecular weight determination by depression of the freezing point of benzene gave 257.

The results of the analysis listed in Table XIII on page 103 were translated to the proportional formula, $C_3H_{24}N_2$. Since this amounted to only 37.43 per cent, the rest was assumed to be oxygen,

which would change the proportional formula to $C_3H_{24}N_2O_9$. It was assumed that the structural formula would be trimethylhydrazine with seven molecules of water. Due to its high affinity to water the hydrazine probably adsorbed the water while it was being sealed in a sample vial. Supplemental analysis showed no trace of lithium or halide in the product. The tetramethylhydrazine was not formed probably because of the steric hinderance to the fourth methyl group.

Recommendations

The following recommendations were derived from the observations made during the course of this investigation.

Preparation of Disubstituted Alkali-metal Amides by the Ziegler Method. Gilman⁽²³⁾ advises against the use of the Ziegler reaction^(74, 75, 76, 77) on a laboratory scale. This advice was born out in this investigation. Nevertheless, if the reaction could be made to proceed, the inherent advantages, as enumerated by Ziegler⁽⁷⁷⁾, would make the investigation worthwhile. Due to the ambiguity of the various translations^(74, 76, 77) of the original patent it was not clear whether the reaction mixture should be refluxed. The statement⁽⁷⁷⁾ that diethyl lithium amide would be obtained as a relatively clear and colorless solution is at variance with experiments made by Gilman and co-workers^(23, 29) and results obtained in the investigation. In order to prepare a dimethyl alkali-metal amide suitable for analysis and electrolysis, a hydrocarbon alkali-metal carrier which may be entirely and easily removed from the product must be used in the reaction.

The problems enumerated above are recommended for further investigation.

Electrolysis of Dimethyl Lithium Amide. A wider range of solvents for dimethyl lithium amide should be investigated. A quantity of product should be prepared sufficient for extensive analysis as to composition and molecular structure.

The electrolysis should be attempted with dimethyl sodium amide, if possible, and the higher disubstituted alkali-metal amides should also be investigated in this manner.

Limitations

The preparation of disubstituted alkali-metal amides was attempted using the procedure of Karl Ziegler^(5,57,58,59), within the following limits:

In this investigation, 0.66 mol of sodium chips were reacted with 0.25 mol of di-n-butyl amine in the presence of 0.25 mol of naphthalene dissolved in 850 milliliters of ether, in a nitrogen atmosphere at 25 °C for 3.25 hours.

Sodium chips, 1.0 mol, were reacted with dimethyl amine in the presence of 0.5 mol of naphthalene, dissolved in 850 milliliters of freshly distilled ether, in a nitrogen atmosphere at 7 °C for 3.5 hours.

Dispersed sodium, 0.5 mol, suspended in 500 milliliters of toluene, was reacted with dimethyl amine in the presence of 1,3 butadiene at -3 °C for 14 hours.

Sodium chips, 0.16 mol, were reacted with dimethyl amine in the presence of 1,3 butadiene in an amine atmosphere at -3°C for 19 hours.

Sodium chips, 1.0 mol, were reacted with dimethyl amine in the presence of 1,3 butadiene in a nitrogen atmosphere at -3°C for 12.0 hours.

Lithium chips, 0.5 mol, were reacted with dimethyl amine in the presence of 1,3 butadiene in an amine atmosphere at -3°C for 3.0 hours.

Lithium chips, 1.0 mol, were reacted with dimethyl amine in the presence of 0.5 mol of naphthalene, dissolved in 850 milliliters of dried and freshly distilled ether, in a nitrogen atmosphere at 7°C for six hours.

Lithium chips, 1.0 mol, were reacted with 1.0 mol of diethyl amine in the presence of 0.5 mol of naphthalene, dissolved in 850 milliliters ether from a container labeled dry ether and also freshly distilled ether, in a nitrogen atmosphere at 35°C for 10 and 2.5 hours respectively.

Diethyl amine, 1.0 mol, dissolved in 1000 milliliters dried and freshly distilled ether, was electrolyzed between a sodium and a platinum electrode in a nitrogen atmosphere at 25°C .

n-Butyllithium was prepared by addition of 0.5 mol of 1-bromobutane, dissolved in 100 milliliters of dried freshly distilled ether, at -5 and -10°C to 1.25 gram atom of cut lithium in 200 milliliters of dried freshly distilled ether in a nitrogen atmosphere over a period of 120 and 35 minutes respectively, with stirring.

n-Butyllithium was also prepared by the addition of 0.5 and 0.75 mol of 1-chlorobutane, dissolved in 100 milliliters of dried and freshly distilled petroleum ether, at 10 and 15 °C to 1.25 and 1.70 gram atom of cut lithium and lithium wire in 200 milliliters of dried freshly distilled ether in a nitrogen atmosphere over a period of 60 and 35 minutes respectively, with stirring.

Dimethyl lithium amide was prepared by passing dimethyl amine into a filtered petroleum ether solution of n-butyllithium against a pressure of 40 millimeters of mercury above atmospheric pressure.

A petroleum ether suspension of dimethyl lithium amide was dried in the absence of air, and dissolved in liquid ammonia with stirring. The ammonia solution of dimethyl lithium amide was electrolyzed between a platinum anode and a mercury cathode, while stirring, at -33 °C, for six, two, and twelve hours respectively.

V. CONCLUSIONS

An investigation of the preparation of disubstituted alkali-metal amides, dimethyl lithium amide in particular, and of the products of their electrolysis led to the following conclusions.

(1) Dimethyl lithium amide could not be prepared, except for trace amounts, on a 0.5 or 1.0 molar scale in the laboratory according to the Ziegler method, by reacting cut lithium with gaseous dimethyl amine in the presence of naphthalene and dry ethyl ether in a nitrogen atmosphere or in the presence of 1,3 butadiene at 25 °C, in a nitrogen or amine atmosphere.

(2) Diethyl lithium amide could not be prepared according to the exact instructions in U. S. Patent 2,141,058 by Ziegler, which state that if cut lithium is reacted with diethyl amine in the presence of naphthalene dissolved in dry ether in an inert atmosphere of dry nitrogen, an almost clear and colorless solution of lithium diethyl amide will result.

(3) Dimethyl sodium amide could not be prepared, except in very poor yield, on a 0.5 or 1.0 molar scale in the laboratory according to the Ziegler method, by reacting cut or dispersed sodium with dimethyl amine in the presence of naphthalene dissolved in dried, freshly distilled ether in an inert atmosphere of nitrogen, or in the presence of 1,3 butadiene.

(4) In the attempted preparations of dimethyl lithium and diethyl amide in an atmosphere of nitrogen, a preferential reaction for the formation of lithium nitride took place even at the low temperature of 25 °C.

(5) In the attempted preparations of the disubstituted alkali-metal amides according to the Ziegler method, if 1,3 butadiene was used, particularly with dispersed alkali-metal, an inseparable mass of tarry substances was formed.

(6) n-Butyllithium was prepared in 94 per cent yield by the reaction of lithium wire in dry petroleum ether with a dry petroleum ether solution of 1-chlorobutane in an inert nitrogen atmosphere at -10 °C.

(7) Dimethyl lithium amide was prepared in 99 per cent yield, based on lithium, by bubbling gaseous dimethyl amine through a filtered petroleum ether solution of n-butyllithium in a nitrogen atmosphere at 25 °C.

(8) A product, analyzed as having the elemental ratio $C_3N_2H_{24}$ and O_9 by difference, a boiling point 74 °C at 715 millimeters of mercury, a specific gravity 0.774 at 25 °C, a molecular weight 257 determined by lowering of the freezing point of benzene, and which acted as a weak base, was obtained as a clear, water white, viscous liquid from the electrolysis of dimethyl lithium amide dissolved in liquid ammonia in a platinum - mercury electrolytic cell.

VI. SUMMARY

The purpose of this investigation was to determine the products of the electrolysis of dimethyl lithium amide.

Preparation of di-substituted alkali-metal amides was attempted by reacting sodium with dimethyl, diethyl, and di-n-butyl amine in the presence of naphthalene dissolved in diethyl ether or in the presence of 1,3 butadiene; lithium with dimethyl and diethyl amine in the presence of naphthalene dissolved in diethyl ether or in the presence of 1,3 butadiene; and butyllithium with dimethyl amine in diethyl or petroleum ether.

After the products were separated, their behavior in air, water, under impact, and at elevated temperature was determined. The products were then analyzed for amine, alkali-metal, carbon, hydrogen, and nitrogen content.

Solubility determinations of dimethyl lithium amide were made, and electrolyses in a mercury - platinum cell in solvents showing solubility were attempted. The product of the electrolyses was analyzed for carbon, hydrogen, and nitrogen content. The specific gravity, equivalent and molecular weights were determined.

Dimethyl lithium amide could not be prepared, except for trace amounts, on a 0.5 or 1.0 molar scale by reacting cut lithium with dimethyl amine in the presence of naphthalene dissolved in ether or in the presence of 1,3 butadiene at 25 °C in a nitrogen or amine atmosphere.

Diethyl lithium amide could not be prepared according to the exact instructions in U. S. Patent 2,441,058 by Ziegler.

Dimethyl sodium amide could not be prepared, except in very poor yield, on a 0.5 and 1.0 molar scale by reacting cut or dispersed sodium with dimethyl amine in the presence of naphthalene dissolved in dried, freshly distilled ether in a nitrogen atmosphere, or in the presence of 1,3 butadiene.

In the attempted preparation of dimethyl and diethyl lithium amide in an atmosphere of nitrogen, a preferential formation of lithium nitride took place even at 25 °C.

n-Butyllithium was prepared in 94 per cent yield by the reaction of lithium wire in dry petroleum ether with a dry petroleum ether solution of 1-chlorobutane in a nitrogen atmosphere at -10 °C.

Dimethyl lithium amide was prepared in 99 per cent yield, based on lithium, by bubbling dimethyl amine through a filtered petroleum ether solution of n-butyllithium at 25 °C.

A product, analyzed as having the elemental ratio $C_3N_2H_{24}$ and O_9 by difference, a boiling point 74 °C at 715 millimeters of mercury, a specific gravity 0.774 at 25 °C, a molecular weight 257 determined by depression of the freezing point of benzene, and which acted as a weak base, was obtained as a clear, water white, viscous liquid from the electrolysis of dimethyl lithium amide dissolved in liquid ammonia in a platinum - mercury electrolytic cell.

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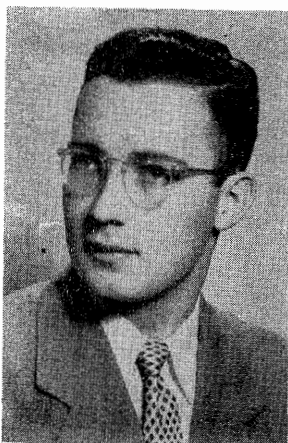
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IX. VITA



The author, Gerhard Gunter Korn, was born in Breslau, Germany on June 11, 1930. He began his elementary school education there in April, 1936. He moved to London, England in August, 1939 and continued school in Dunstable, England from October to March, 1940. He moved to New York in April, 1940 and from there to Annapolis, Maryland where his schooling was continued. In October, 1940 he moved to Norfolk, Virginia, where his elementary schooling was completed.

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