PROCEDURE IN THE SYNTHESIS OF ETHYLLITHIUM IN AN ATMOSPHERE OF ARGON

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T. V. Talalaeva and K. A. Kocheshkov

L. Ya. Karpov Physicochemical Institute

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In the synthesis of compounds which decompose on access of air the work is often carried out in an atmosphere of an inert gas. Dry nitrogen which has been freed from oxygen is usually used, but in recent years helium and argon have come more and more into use. The advantage of the use of helium and argon is clearly seen, for example, in the synthesis of a Grignard reagent: the yield of RMgX is then close to quantitative and the Wurtz-condensation side reaction is reduced to a minimum [1]. Excellent results in work in an atmosphere of helium have been reported also for the preparation of solutions of organolithium compounds [2].

The methods for the preparation and isolation of crystalline organolithium compounds in argon may find application in a great variety of syntheses of organometallic compounds. As an example of the procedure that we use in this work we describe the synthesis of ethyllithium from ethyl chloride in benzene. Despite the large number of investigations, both Soviet [3-5] and foreign [6-10], carried out with ethyllithium, detailed descriptions of synthesis procedures have not been given. The description that we have already given [11] of the synthesis of pure ethyllithium from ethyl bromide and lithium in an isopentene medium with subsequent replacement of solvent probably remains the sole detailed description of procedure and has therefore been used by a number of authors for the synthesis of pure ethyllithium [5, 6, 7, 12, 13].

EXPERIMENTAL

For the preparation of crystalline ethyllithium we use "cryoscopic" benzene and pure hexane and pentane, distilled and dried over sodium in an atmosphere of argon. Solvents are not poured out of vessels, but are siphoned out under a pressure of argon or taken by pipets that have been filled beforehand with argon (30-, 50-, 100-, and 150-ml pipets were used). All apparatus is first dried at 200-230° and purged with argon. Ground joints are greased at the upper edge with the usual vacuum grease. Lithium, in the form of thin plates (1-2 mm), is cleaned to remove oxide film and cut up as finely as possible under argon in a chamber above a wide-necked vessel, which has also been purged with argon. The vessel is closed with an ordinary rubber bung. The small pieces of lithium obtained in this way remain bright for one or two days. Lithium may be comminuted by heating it in a round-bottomed, thick-walled flask under argon in boiling dodecane until it is all melted and then shaking to break it up. The bright suspension of lithium is washed rapidly with hexane and benzene and is transferred to the reaction flask using a system of adapters with ground glass joints.

For the synthesis of ethyllithium, lithium with the usual specification is used (Na content 0.02-0.05%), because the reaction between pure lithium and alkyl chlorides is extremely sluggish. It is interesting that with the lithium-6 isotope (isotope content 95%) the reaction with ethyl chloride is very vigorous and gives a yield of ethyllithium in solution of up to 85%.

All work with ethyllithium solutions and with crystalline ethyllithium is carried out under a small positive pressure of argon. Special precautions must be taken in work with crystalline ethyllithium. It is necessary to work in a mask of "organic glass" or in good protective goggles.

Preparation of a Benzene Solution of Ethyllithium from Ethyl Chloride. The apparatus consists of a 1-liter flask with five necks (Fig. 1) fitted with stirrer, gas-inlet tube (it serves later as a siphon), reflux condenser connected

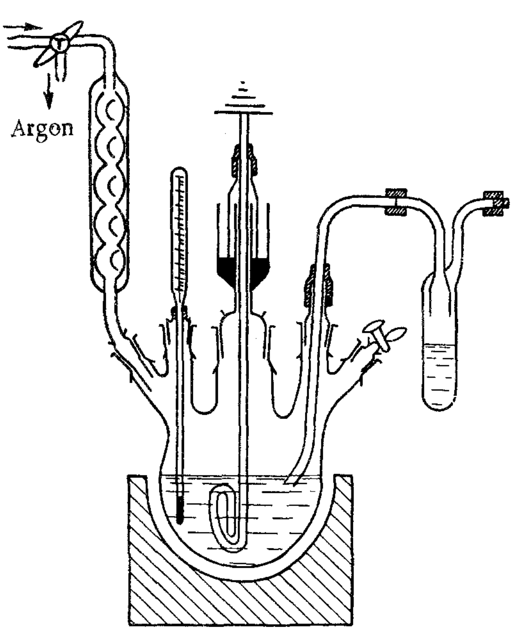

Fig. 1.

through a three-way tap to the argon supply, thermometer, and safety tap. Before use the apparatus is dried at 200-230° and purged with argon through the siphon; the argon supply is then connected to the three-way tap on the condenser. About 500 ml of benzene is introduced through the siphon, and 12 g of small pieces of lithium in a vessel under argon is wetted with 10-15 ml of benzene. A funnel with a wide stem is placed in the neck used for the siphon, and through this, in a brisk counter current of argon, lithium is rapidly transferred into the flask. The siphon is inserted and raised so that it almost touches the surface of the benzene, and it is connected to a trap containing ethyl chloride. For this amount of lithium we take two ampoules of commercial ethyl chloride (about 50 g); before it is poured into the trap, the ethyl chloride is cooled. The reaction mixture is heated to 40°, 2-3 ml of ethyl chloride is added immediately, and then the passage of gaseous ethyl chloride is started (with vigorous stirring).

Reaction usually starts after about five minutes. The temperature of the reaction mixture is kept in the range 45-55° (it is sometimes necessary to apply cooling). A grayish turbidity rapidly makes its appearance, and pieces of lithium fall into the lower part of the solution. The passage of ethyl chloride occupies 2.5-3 hours. The solution is stirred further for 2.5-3 hours at 45-50°. The mixture is then siphoned out under a pressure of argon (the siphon is lowered to the bottom) into an ordinary stoppered 500-ml thick-walled measuring cylinder (see Fig. 2), which has first been dried and purged with argon. The cylinder is disconnected from the apparatus, and the solution is allowed to cool in a stream of argon. It is then closed rapidly with a rubber (not glass!) stopper and is further protected with two rubber caps. The glass cylinder is placed in a protective metal cylinder, and the solution is left to settle until it is clear, which usually requires one day — rarely two.

As soon as the siphon is disconnected from the apparatus, the funnel is inserted rapidly and 200-250 ml of ordinary benzene is added. The stirrer is removed and the necks are stoppered. The residues of the reaction mixture are poured onto sand in an allotted place outside. The decomposition of the residues in the reaction flask may be carried out with a 1 : 1 mixture of alcohol and benzene, but this is less convenient and more dangerous. The colorless benzene solution of ethyllithium obtained after settling usually has a concentration of 0.85-0.95 N, i. e. the yield is 70-85%. The clear solution may be siphoned under a pressure of argon into any required apparatus, either all at once, or in portions. From such a solution (about 500 ml) 8-10 g of crystalline ethyllithium can be isolated (yield up to 45%).

Preparation of Crystalline Ethyllithium. When solvent is driven off it is convenient to use a magnetic stirrer, which ensures steady boiling. Benzene may be distilled off under somewhat reduced pressure. There is scarcely any difference in the yields of crystalline ethyllithium when distillation is effected by applying heat and when it is carried out in a vacuum, because under these conditions the losses due to the thermal decomposition of ethyllithium are low. The clear benzene solution of ethyllithium (~500 ml; 0.80–0.95N), obtained after the settling of the solution is siphoned under a pressure of argon into a distillation apparatus, about 700-750 ml in volume (Fig. 2), filled with argon. This is then connected, in a stream of argon, to a condenser with receiver, and it is warmed cautiously so that 400-425 ml of benzene distills off (down to a volume of 75-100 ml). The residue is diluted with an equal, or somewhat greater, volume of dry pentane or hexane, and it is filtered in argon through a dry folded filter. Should crystals be precipitated, the solution must be warmed slightly and filtered warm through a funnel for hot filtration. For the receiver we use an ordinary 350-ml reaction vessel (Fig. 3). A completely clear colorless filtrate is obtained. Then, very rapidly and cautiously, without stopping the stream of argon, the funnel and filter are disconnected and closed at the lower end; the receiver is closed by means of a cap. The funnel is transferred to a draft cupboard, the stopper is removed, and the filter burns up explosively. At this stage the filtrates from two experiments may be combined and treated together. The solution is cooled to −20° without stopping the stream of argon, and the crystals of ethyllithium are separated (10-20 g). The filtration is carried out in the apparatus portrayed in Fig. 4, which is first dried and purged with argon. The apparatus and filter (No. 2) are made of molybdenum glass. The apparatus for filtration and drying in a vacuum (Fig. 5b) must be checked before use, because with the slightest influx of air pure ethyllithium burns explosively.

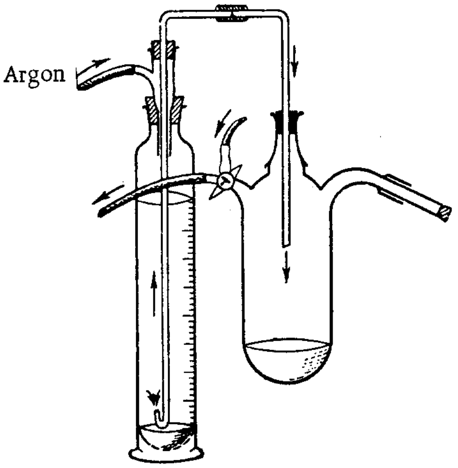

Fig. 2.

The suspended precipitate is readily transferred onto the filter (connecting tubes of internal diameter of not less than 10-12 mm). The precipitate is washed twice on the filter with pentane or hexane, cooled to −10° with gentle suction through a Tishchenko vessel with the aid of a rubber bulb. The apparatus is closed, and the precipitate is dried at a reduced pressure of 2-3 mm for 15-30 min; the vacuum is broken with argon (Fig. 5b). From one experiment we usually obtain 8-10 g of crystalline ethyllithium, and when two experiments are run together – 16-20 g of ethyllithium. The ethyllithium is then distributed into ampoules in argon (Fig. 5a). The ampoules are then weighed, and their tips are capped with a layer of wax. They are kept in a vertical position in asbestos sheaths in a metal vessel filled with argon.

If a large amount of ethyllithium (5-10 g) is sealed in an ampoule, it can be dispensed in a stream of argon with the use of a fairly simple device (Fig. 5c). To transfer the whole of the substance from the ampoule to an apparatus for dissolution the device shown in Fig. 5c can again be used. At the end at which the ampoule is to be attached the device is closed with a stopper, and it is carefully purged with argon. The ampoule filled with argon is opened in the vertical position and the device is immediately attached to it in a counter current of argon. With continued passage of argon the second end of the device is lowered 5-10 cm into the neck of the apparatus, also in a counter current of argon, going both through the device and through the apparatus (from two directions). The ethyllithium is transferred directly into the solvent. The apparatus is closed and shaken or warmed slightly to bring about dissolution.

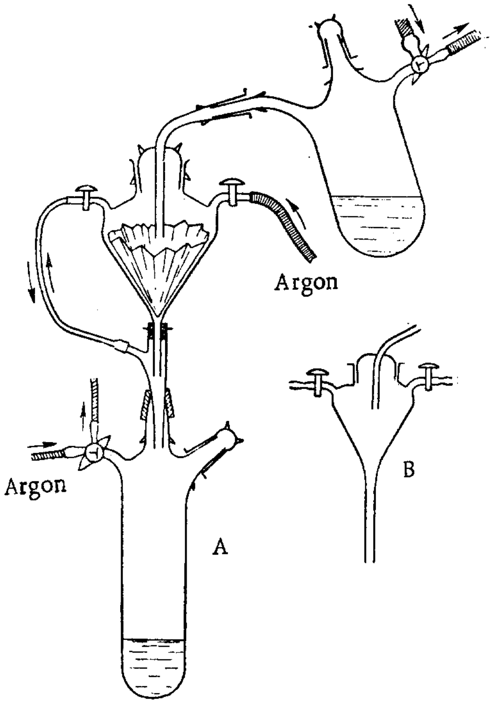

Fig. 3.

To obtain pure ethyllithium it is crystallized once or twice from hexane under argon; it may be crystallized also from benzene, cyclohexane, or cyclohexene. In alkylbenzenes (xylene, mesitylene, toluene) solutions of ethyllithium are unstable, particularly to heat [14]. In the dissolution of 10-15 g of ethyllithium that has been kept in a sealed ampoule under argon, there is always a slight turbidity, sometimes noticeable only by transmitted light. The solution is therefore warmed to 40-50° and filtered warm under argon through a dry fluted filter, which has been dried over phosphorus pentoxide in argon. After filtration a colorless and completely clear solution of ethyllithium is obtained. From hexane, crystals of ethyllithium are obtained by cooling to −20°, vacuum-dried, and dispensed into ampoules as indicated above. Freshly recrystallized ethyllithium gives a clear solution, almost free from any impurities. For the analysis of such a solution it is sufficient to titrate with acid after the decomposition of an aliquot part of the solution with water. A double titration with benzyl chloride [15] does not give the residual alkalinity if the benzyl chloride used is vacuum-distilled over phosphorus pentachloride and kept over calcium chloride in argon. Carefully purified ether is distilled and kept over sodium under argon. For a solution of pure ethyllithium the control reaction with benzophenone gives a quantitative yield of α-ethylbenzhydrol.

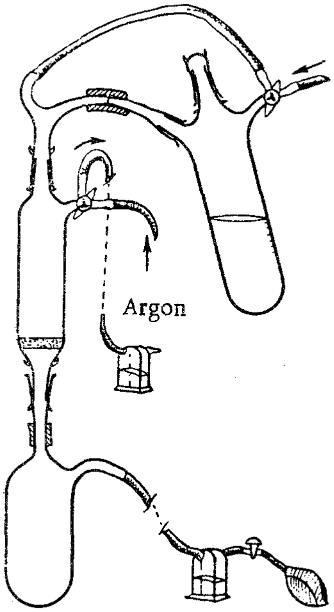

Fig. 4

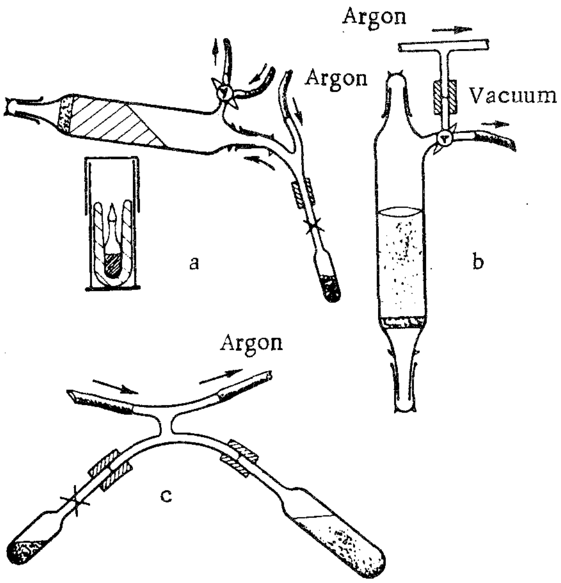

Fig. 5

Analyses of a solution of pure ethyllithium carried out by titrating a test sample with acid agree within the limits of experimental error with the volumetric determination of ethane liberated in the hydrolysis of an equal portion of the solution [cf. 4, 16]. The analysis of crystalline ethyllithium is carried out essentially in the same way. A weighed amount of ethyllithium (sealed in an ampoule under argon) is dissolved by breaking the ampoule under solvent in an atmosphere of argon, and the analysis is then carried out by one of the methods indicated above [11].

Very pure ethyllithium can be prepared by vacuum sublimation without the use of crystallization. The sublimed ethyllithium obtained is brought into solution and analyzed in solution. The taking of a sample of sublimed ethyllithium is fairly difficult, for it sticks very firmly to the walls of the ampoule, which makes manipulation difficult. Regarding the sublimation of ethyllithium see also [8, 16]. For examples of the analysis of crystalline ethyllithium and the isotope-substituted compounds C_2H_5Li-6, CH_3CD_2Li, CD_3CH_2Li and C_2D_5Li see [17]. The synthesis of these compounds was carried out by the above-described method.

SUMMARY

The procedure in the synthesis of ethyllithium in an atmosphere of argon is described.

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