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PREPARATION OF TERT-BUTYLLITHIUM

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Summary

A detailed investigation of the effect of reaction conditions on the yield of t-butyllithium in pentane is reported. Dependable yields of 70% to 80% are obtained under optimum conditions.

Introduction

This paper describes the results of an investigation to determine the effects of various reaction parameters on yield, and the optimum, most dependable conditions for the preparation of t-butyllithium from t-butyl chloride and lithium metal in hydrocarbon solvents (eqn. 1).

$$t\text{-}C_4H_9Cl + 2Li \rightarrow t\text{-}C_4H_9Li + LiCl \qquad (1)$$

Although a number of the conditions that we found necessary for maximum yield have been reported by other investigators [1—11], we would like to confirm these conditions and point out several other conditions which are also critical.

The maximum yields that were obtained in this work were approximately 80%, in agreement with Kamieņski and Esmay [8], and usually ranged from 70 to 80% depending on the care used.

Results

Low and variable yields of t-butyllithium occurred initially in this investigation and are attributed to side reaction 2, that of unreacted t-butyl chloride with t-butyllithium, because of the heavy white precipitate of lithium chloride often found in filtered preparations after standing.

$$t\text{-}C_4H_9Li + t\text{-}C_4H_9Cl \rightarrow LiCl + \text{hydrocarbon products} \qquad (2)$$

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The rate of the heterogenous reaction 1 must be maximized to minimize the loss of yield due to the homogeneous reaction 2 which proceeds in competition. Various parameters were changed systematically to ascertain their effect on yield. Only one parameter was changed at a time, and a standardized comparison was determined by total base titration. The correction factor for non-carbon bound base ran 2% of the t-butyllithium. All reactions were run under argon. (Nitrogen should not be used because of deactivation of the metal due to nitride formation.)

Effect of metal. No reaction of t-butyl chloride in pentane was observed when pure lithium metal (0.02% sodium) or pure sodium metal powder was used. All sodium—lithium metal powders used were 40 to 80 microns in size.

The 1.0% sodium—lithium alloys gave up to 5% higher yields than those containing 0.5% or 2.0% sodium. The presence of copper metal powder did not affect the yield. Coarser dispersions or obviously contaminated metal caused the yield to fall off drastically.

The reaction (initiation) starts readily in a few minutes when fresh metal, vigorous stirring and refluxing pentane are used.

Effect of solvent. All solvents were dried over sodium wire. Lower boiling hydrocarbon solvents such as pure isopentane and n-pentane gave good yields. Higher reflux temperatures increase the rate of reaction 2 but have much less effect on reaction 1. For instance, the use of hexane or hexane—isopentane (reflux 45°C) produced low yields, (0-30%), with severe coupling. n-Pentane was chosen as the preferred solvent, although isopentane gave a 1% higher yield under comparable conditions due to its lower boiling point. When conditions are not optimum, e.g. dispersion metal not fresh, the presence of about 20% isopentane in the pentane increased the yield by 10 to 15%.

There was no difference in yield between dry distilled olefin-free pentane and dry commercial pentane. There was no change in yield when a few percent 2-pentene was added, but a few percent 1-pentene did cause a significant increase in yield. This is probably due to the solubilizing effect on the metal surface of the primary alkyllithium compound formed from the addition of t-butyllithium to the 1-pentene.

Effect of t-butyl chloride. Addition of a small amount of t-butyl alcohol to the t-butyl chloride improved yields from 40% up to 80% t-butyllithium, 0.5% by weight being optimum. The amount of t-butyl alcohol initially present varied from 0.0% to 0.3% depending on the method of purification and source. The effect of t-butyl alcohol must be a sort of solubilizing agent in the form of lithium t-butoxide interacting with the t-butyllithium or the lithium chloride as it forms on the surface of the lithium metal. Washing the sodium—lithium dispersion with dilute t-butyl alcohol in hexane did not give an enhanced increase in yield when used with t-butyl chloride (free of t-butyl alcohol). (It is possible that the presence of small quantities of air during the reaction, leading to the formation of lithium t-butoxide, may have helped some investigators obtain increased yields and provided erratic yields for others.) In another experiment, the addition of an equivalent amount of 0.5% t-butyl alcohol after two-thirds of the t-butyl chloride was added gave a 10% lower yield than if all the alcohol were present initially. Dilution of the t-butyl chloride (0.5% t-butyl alcohol) with pentane and then addition to the pentane—lithium metal slurry gave a 1% to 3% decrease in yield.

Addition of 0.5% by weight of n-butyl alcohol or sec-butyl alcohol had about the same effect as t-butyl alcohol.

Laboratory yields of n-butyllithium and sec-butyllithium in hexane in our laboratories are usually 90-96% with no alcohol present in the starting alkyl chlorides. Therefore, this same effect of the alcohol or alkoxide is not present in the normal or secondary systems.

Virtually no change in yield was noticed in running the reaction at different product concentrations varying from 16 to 25% by weight solution. A slight decrease was noted in dropping to about 8% concentration.

The reaction of t-amyl chloride (0.5% t-amyl alcohol) with 1.0% sodium—lithium dispersion using the optimum conditions determined for t-butyllithium gave only coupling products and lithium chloride. The preparation of 1-norbornyllithium in pentane proceeded readily under these conditions.

Other effects. An addition time of 2.5 to 3 h for t-butyl chloride was found to be convenient for laboratory scale, and produced optimum yield. This rate of addition produced a steady reflux which is important to maintain. Addition times shorter than 0.75 h will cause a decrease in yield.

A 20% to 25% excess of metal was found to give the optimum yield.

The reaction is exothermic up to the end of the t-butyl chloride addition, and then it is allowed to cool gradually for two hours with stirring to insure complete reaction of the t-butyl chloride before filtration.

Vigorous stirring was found to be beneficial. An increase of 12% in yield was found between conditions where the slurry was just agitated for reasonable mixing and where a high-speed agitator was used.

Stability. Less than 0.5% of the contained t-butyllithium decomposed in five months at 30° as a 12% solution in pentane. Actually t-butyllithium is about four times more stable than n-butyllithium at room temperature [12]. Decomposition rates of t-butyllithium at higher temperatures may involve other mechanisms [13].

Experimental

Materials. The hydrocarbon solvents were obtained from Phillips Petroleum and dried over sodium wire. The purified pentane was washed with concentrated sulfuric acid, then water, dried over molecular sieves and distilled to give olefin-free material. The t-butyl chloride was obtained from Eastman Organic, and Matheson, Coleman and Bell.

Analyses for t-butyl alcohol were determined by GLC on a 5 ft, 15% SE-30 column. All reactions and handling of lithium metal powders were performed under argon.

Preparation of lithium metal dispersion

The 1.2% Na—Li metal dispersions were prepared by adding 250 g of 1,2% Na—Li metal, 750 ml Soltrol 170 (Phillips) (either rod, ribbon, or wire) and 3-4 ml of commercial oleic acid to a 2-l stainless steel, 3-neck flask. Additional sodium metal can also be added at this point to adjust the actual sodium content. (Molten lithium metal will rapidly attack glass causing breakage as soon as it "wets" the glass surface. Therefore, the use of glass flasks is dangerous, although it has been done successfully.)

The flask is equipped with a Stir-O-Vac stirrer (Cole—Parmer) or any high-speed, high-shear stirrer, metal thermocouple, and glass reflux condenser (used as an air condenser—no water). The entire apparatus is maintained under an argon atmosphere but kept at approximately atmospheric pressure by means of an oil leg-bubbler. (Nitrogen will react with lithium metal. All operations with lithium metal dispersions should be under argon or helium to maintain the maximum reactivity of the dispersion and for safety.)

The flask is heated with minimum stirring until the lithium metal (m.p. 182°) has definitely melted (about 200°), and stirring increased to 2000 r.p.m. (or as high as possible). Heating is continued until the temperature rises to about 210-215°. The flask is held at this temperature for 5-10 min with maximum stirring possible. The heat is removed, stirring immediately stopped and the outside of the flask quenched with a dry ice/heptane bath as rapidly as possible. When the temperature has fallen to about 90°, stirring is resumed to obtain even cooling. When the dispersion reaches room temperature, it is transferred and filtered under argon, washed with Na-dried pentane three times, and blown dry with argon. Conical glass filters with a fritted glass disc and ball socket ground-glass joints as supplied by Ace Glass Co. were satisfactory for filtration. The powder is ready for use. (Caution: The dry powder can be pyrophoric in moderate quantities if high humidity air comes into contact with it.)

Recommended laboratory procedure for preparing t-butyllithium

A 3-necked, round bottom flask equipped with a high-speed stirrer (Stir-O-Vac, Cole—Parmer) or any high-speed, high-shear stirrer, pressure-equalizing dropping funnel and reflux condenser, was flushed with argon thoroughly, and then 470 ml sodium-dried pentane and 17.0 g 1% sodium—lithium alloy dispersion added. (Spherical ground joints with clamps are preferred for these preparations because of safety considerations.) The pentane slurry was heated to reflux and stirred vigorously, and then the addition of 107 ml (0.979 mol) t-butyl chloride containing 0.5 ml t-butyl alcohol was begun. The reaction began after 3 to 5 ml was added. (If the reaction does not start after 12 ml have been added, do not add more t-butyl chloride until the reaction has initiated.) The addition took 3.0 h and maintained a moderate reflux without external heating. After the addition was finished, the slurry was permitted to cool gradually with vigorous stirring for 2 h more. The reaction slurry was then filtered under argon pressure through an "E" (4 to 8 microns) sintered glass conical filter. (Filtration was rapid.) The reaction flask was rinsed with 200 ml fresh pentane which was then poured through the filter cake as a rinse. The combined pentane solution was 10.95% in total base with 0.25% Gilman correction [14] to give a net 10.7% t-butyllithium solution weighing 475 g. The overall net yield was 80%. (Yields will vary from 70-81%.) (Caution: washed filter cake is pyrophoric.)

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