PREPARATION OF VINYLLITHIUM

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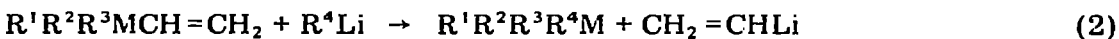
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Summary

A thorough investigation of the effect of reaction conditions on the direct formation of vinyllithium from vinyl chloride and lithium metal in tetrahydrofuran is reported. Under optimum conditions yields of 69 to 79% were dependably obtained.

Introduction

There have been a number of attempts to prepare vinyllithium directly from lithium metal and vinyl chloride (eqn. 1) [1-5], but only one of these has been considered dependable [3].

$$CH_2 = CHCl + 2Li \rightarrow CH_2 = CHLi + LiCl \tag{1}$$
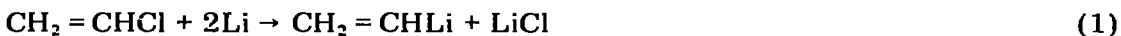
Even this procedure gave only a low concentration with some question as to the amount of other impurities present. The only practical preparations of pure vinyllithium have been the exchange reactions between a vinyltin, vinyllead or vinylmercury derivative and organolithium compounds (eqn. 2) or lithium metal (eqn. 3) [6-10].

$$R^1R^2R^3MCH = CH_2 + R^4Li \rightarrow R^1R^2R^3R^4M + CH_2 = CHLi \tag{2}$$

$$(CH_2 = CH)_xM + xLi \rightarrow M + xCH_2 = CHLi \tag{3}$$

(M = Sn, Pb, Hg; R = alkyl, aryl or vinyl)

The direct formation of vinyllithium by reaction 1 would provide the most convenient route if the reaction proceeded dependably with reasonable purity, concentration and yield. A detailed examination of the various reaction parameters was therefore carried out.

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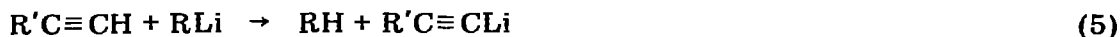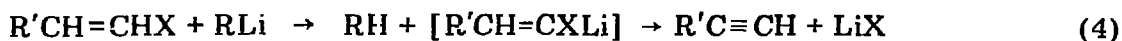
Results

Analytical. The analyses of C_2H_3Li in THF solutions were initially perform-ed by reaction with vanadium pentoxide [2, 14], but the Gilman procedure used for n-butyllithium [15] was found to be far more accurate and dependable when allyl bromide was used as the coupling reagent instead of benzyl chloride. (A standard solution of vinyllithium from tetravinyltin, and containing lithium butoxide, gave good checks with the calculated amount.) The amount of Gilman correction usually ran about 10-15% of the total base titration. Under the con-ditions of the analysis, lithium acetylide does not react with the allyl bromide.

Effect of solvent. The reaction of vinyl chloride and 1% sodium—lithium metal powder initiated, but did not proceed in pure ether. Low yields were obtained in THF/diethyl ether mixtures. Although a reaction occurred in 1,2-dimethoxy-ethane at $-25°C$, the slurry solidified or polymerized on warming to $0°$. The reaction initiated as low as $-30°$, and proceeded readily in THF; and this was chosen as the optimum solvent.

Effect of temperature. In runs where the product concentration was less than $0.5\ M$, only small differences were noted with temperature; but on preparing more concentrated solutions, the yield and purity increase with lower tempera-tures. For example, the yield for nominal $2\ M$ reactions run at $0°$ was 28%; at $-20°$, 65%; at $-28°$ to $-31°$, 73%; and at $-31°$ to $-34°$, 78%.

The minimum amount of impurities was also obtained at the lowest tem-perature, $-31°$ to $-34°$; about 11% of the total base calculated as vinyllithium. During the reaction $2\ M$ vinyllithium solutions thicken greatly at temperatures lower than $-35°$, with the yield actually falling off. If the reaction is run so that a product concentration of $1\ M$ is obtained, the reaction temperature can be lowered to $-60°$, but only a 5% increase in yield results.

Side reactions. The main side reaction (eqns. 4 and 5) is similar to the reaction reported for substituted vinyl chlorides [11-13], and for vinyl bromide [5].

$$R'CH=CHX + RLi \rightarrow RH + [R'CH=CXLi] \rightarrow R'C\equiv CH + LiX \qquad (4)$$

$$R'C\equiv CH + RLi \rightarrow RH + R'C\equiv CLi \qquad (5)$$

($R' =$ alkyl, aromatic or hydrogen; $R =$ vinyl or substituted vinyl; $X =$ Cl, Br)

The calculated amount of ethylene was evolved (IR) according to equation 6 when a two-fold excess of vinyl chloride was added to 1% sodium—lithium dis-persion in THF at $-35°$. The acetylene reacted further to form lithium acetylide

$$CH_2=CHLi + CH_2=CHCl \rightarrow CH_2=CH_2 + LiCl + HC\equiv CH \qquad (6)$$
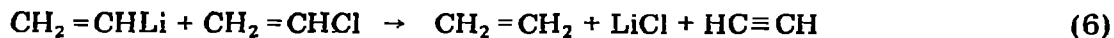
or carbide. The solution and precipitate contained at least 80% of the calculated amount of lithium chloride. Ethylene was also found to be evolved near the end of normal reactions in forming vinyllithium (65% product yield).

If a vinyllithium product slurry is filtered while still cold after the reaction has been completed, having never been warmed above $-20°$, a clear solution results which instantly precipitates lithium chloride on warming, indicating the presence of some unstable intermediate compound decomposing to lithium chloride, such as α-lithiovinyl chloride. Therefore, the product solution is al-

lowed to warm to room temperature, and stand for several hours, before filtration. This technique also improves the filtration rate of the slurry.

Hydrolysis of filtered vinyllithium solutions indicated (IR) only two gases were formed; ethylene with a small amount of acetylene. Organic extraction of the aqueous hydrolysis solution produced a trace of an unsaturated alcohol but no other products or polymer. Therefore, the only significant impurity in these vinyllithium solutions is lithium acetylide, solubilized in solution by the vinyl-lithium. (Lithium carbide is not soluble in organics as Li_2C_2.)

About two-thirds of the Gilman correction factor is estimated to be due to solubilized lithium acetylide. (Estimated by carrying the reaction to a few percent of completion and then analyzing for total non-carbon lithium base present (Gilman correction).) This correction factor was assumed to be solely due to the impurities in the starting materials and was about one-third of the final Gilman correction usually found in the product solutions. This agrees with the GLC determination of 0.08 for the ratio of lithium acetylide to vinyl-lithium using the trimethylsilyl chloride derivatives. This ratio was lowered to 0.01 by heating the product slurry to 60° for 3 min, cooling, then filtering. The addition of hexane or diethyl ether had only a slight effect on this ratio.

Starting materials. The reaction of vinyl chloride initiated in three to five minutes at −20°, but the addition of about 4 ml of a preformed vinyllithium/THF solution eliminated the induction period. Vinyl bromide gave only 8% yield under the same conditions (and less in diethyl ether), in approximate agreement with previous workers [5]. Purified THF was preferred for the reaction, although commercial THF (inhibited) from freshly-opened containers (> 99.5%) was also satisfactory.

Lithium metal powder containing 1.0 to 2.0% sodium was optimum with as fine a particle size as possible (40-80 microns), but coarser powder does give satisfactory results. Pure lithium (no sodium) dispersion did not form the product.

The optimum excess of metal was 20%, with larger excesses causing a slight decrease in yield. Older sodium—lithium metal dispersions, although shiny in appearance, caused some 5% falling off in yield.

Other factors. It is important to have high-speed stirring especially with good shear action. The yield dropped from 76% to 54% while the percent Gilman correction to total base doubled to 30% when the stirring was slowed to a point to just agitate and stir the reaction slurry. Good stirring also promotes good temperature control since the reaction slurries have the tendency to freeze to the sides of the flask, causing improper mixing.

The more concentrated the reactions were run, the higher the yield and purity: a final concentration of 2.0 M gave 74%; 1.1 M gave 67%; and 0.5 M gave 65% in one set of experiments.

The optimum rate of addition of vinyl chloride to the reaction mixture was about 1.0 to 1.5 h. Addition times shorter than about 0.75 h and longer than about 2 h caused some 3 to 10% decrease in yields. If the vinyl chloride is added faster than it can react with the metal, it will react with the vinyl-lithium. If it is reacted too slowly, the metal evidently becomes coated with some lithium chloride and by-products which precipitate out. It was preferable to gradually slow down the rate of addition of vinyl chloride as the reaction proceeded.

Vinyllithium product solution. The product solution ranged in color from yellow to reddish-orange. Darker colors occurred when oxygen contamination wa; more than usual. The solutions resulting from the experimental procedure in this re port ranged about 1.9-2.1 M, or about 7.3% by weight net vinyllithium in THF solu tion containing 6.5% lithium chloride; almost a 1/1 complex. The Gilman correction (non-carbon soluble base) was 10 to 14% of the total base concentration. If two-thirds of this correction is lithium acetylide, then the lithium acetylide/ vinyllithium ratio is about 0.10 (0.08 by GLC). Although the solutions are highly air sensitive, they were not pyrophoric.

Stability. THF solutions of vinyllithium slightly darken more on standing at room temperature, but are not greatly colored even after four months. The products of THF cleavage are THF-soluble, but there is also a slow build-up of pre-sure, probably due to ethylene formation.

At 30° an initial 6.63% vinyllithium in THF solution decomposed to: 6.53% in 7 days; 6.02% in 21 days; 5.31% in 35 days. The decomposition rate increased about three-fold on increasing the temperature to 40°. (This rate of decomposition is comparable to that of 20% phenyllithium in 75/25 benzene/ether [16].) Obviously, these solutions should be stored at 0° if not used immediately.

Experimental

General. The THF was DuPont commercial, anhydrous grade, and was distilled from $LiAlH_4$ under vacuum to 20% remaining volume (never to dryness). Vinyl chlor-ide was supplied by Matheson Gas Products. Lithium metal powders containing var-ious amounts of sodium were made in a high-speed disperser in mineral oil under ar-gon. All reactions and products were handled under argon. (See ref. 17 for prepara-tion of lithium metal dispersion.)

The same general experimental set-up was used for all runs to examine the ef fect of the various reaction parameters. After complete reaction, the product slur-ry was filtered and analyzed for total base and for non-carbon bound lithium base. The yield was then calculated on actual vinyllithium content.

Preparation of vinyllithium. To a 3-l, 3-necked, round bottomed flask, purged with argon, equipped with a high-speed stirrer (Stir-O-Vac, Cole—Parmer, or any high-speed, high-shear stirrer), a dry ice reflux condenser, a gas addition tube and a low temperature thermometer, was added 77.7 g of 1.2% sodium—lithium alloy powder and 1750 ml of THF. The slurry was stirred while maintaining a slight positive argon atmosphere by means of an oil-filled bubbler. The dry ice con-denser was cooled to —78° and the THF slurry to —20° and stabilized. The vinyl chloride from a small weighed cylinder was admitted above the surface of the slurry for 1.6 min (approximately 3.0 g) and then turned off. The slurry was stirred vigorously until a rapid 4° rise in temperature was observed. (The induction period is 10 min with unpurified THF, and it is usually 3 to 5 min for purified THF.) The slurry was cooled immediately to —34° and the vinyl chloride again added. The graduated rate of addition was as follows: after 0.5 h, 106 g; after 1.0 h, 185 g; after 1.5 h, 263 g; after 1.8 h, 291 g in total. The tempera-ture was maintained at —31° to —34° during the addition. The product slurry was allowed to warm slowly to —5° over 2 h. The reaction flask was capped, re-moved from the low temperature bath and permitted to warm to room tempera-

ture overnight and filtered through a conical sintered glass filter (E porosity, 4-8 microns) under argon pressure and analyzed by the Gilman double titration procedure, using distilled allyl bromide as the coupling agent for the vinyllithium [15]. (Benzyl bromide may also be used.) (The filter cake is highly reactive but not usually pyrophoric.)

The clear light orange-yellow solution weighed 1646 g and analyzed net as 2.06 M or 7.31% by weight vinyllithium with a Gilman to total base ratio of 10.8%. The yield was 76.4% based on vinyl chloride.

Acknowledgement

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