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A New Metalation Complex for Organic Synthesis and Polymerization Reactions

A new organometallic complex of N,N,N',N'-tetramethylethylenediamine (TMEDA) and lithium has been prepared on a laboratory scale. The complex shows promise as a metalation intermediate for the controlled synthesis of aromatic organic compounds and the formation of polymers. The complex of TMEDA and lithium can also be used for the preparation of various organo-lithium compounds. One such compound, benzyllithium ($C_6H_5CH_2Li$), an effective metalation agent itself, is relatively expensive. A number of other organometallic compounds, which are readily available at moderate cost, are generally limited to specific types of reactions.

The new complex, TMEDA-Li•TMEDA, is easily prepared by reacting butyllithium (BuLi) and an excess of TMEDA in an inert solvent (e.g., hexane) at room temperature for approximately six hours, in accordance with the following sequence of reactions:

(1) $BuLi + TMEDA \rightarrow BuLi\cdot TMEDA$

(2) $BuLi\cdot TMEDA + TMEDA \rightarrow TMEDA\text{-}Li\cdot TMEDA + C_4H_{10}$

The butane (C_4H_{10}) formed in the second step is evolved as a gas and provides a quantitative indication of the completion of the reaction sequence. The complex product TMEDA-Li•TMEDA cannot be readily isolated in the free state, as it is decomposed by water and other hydrolytic solvents. However, its potential as a metalation agent for aromatic hydrocarbons has been demonstrated by using the hexane solution of the complex (obtained in the two-step reaction sequence) to convert toluene ($C_6H_5CH_3$) into benzyllithium ($C_6H_5CH_2Li$). This conversion was accomplished by adding toluene to the TMEDA-Li•TMEDA solution and allowing the mixture to react for approximately 17 hours. The reaction proceeded in accordance with the following equation:

$$TMEDA\text{-}Li\cdot TMEDA + C_6H_5CH_3 \rightarrow C_6H_5CH_2Li + 2TMEDA$$

The effectiveness of the TMEDA-Li•TMEDA complex as an initiator for polymerization was demonstrated by adding butadiene to a separate portion of the hexane solution of the complex cooled to 273 K (0° C). After 20 minutes, methanol was added to terminate the reaction. The reaction mixture was then acidified and diluted with hexane, and the hexane layer containing the polymer was washed with water and decanted. The polymer, a soft solid, was isolated by evaporating the hexane.

Note:

Requests for further information may be directed to:

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Patent status:

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