

The Effect of HMPA on the Reactivity of Epoxides, Aziridines and Alkyl Halides with Organolithium Reagents.

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Supporting Information

General Experimental Conditions for Bis(phenylthio)methylithium Kinetics. A 25 mL volumetric flask was oven dried and cooled either in a desiccator under N₂ or by purging while hot by blowing a stream of argon into the bottom of the flask. Bis(phenylthio)methane (~1.3 mmol) was weighed in. The flask was capped with a septum, sealed with parafilm, and purged with argon. Dodecane (~1.0 mmol) was weighed into the flask. The volumetric flask was filled with freshly distilled THF and weighed, and the concentration was determined. The stock solution was kept no longer than 2 days. Four long-neck^[S-1] 5 mL round bottom flasks and stir bars were oven dried and cooled in a desiccator under N₂. After cooling, the flasks were capped with septa, labeled, sealed with parafilm, purged with N₂, and placed under positive N₂ pressure. Bis(phenylthio)methane/dodecane stock solution (3 mL) was added to each flask. The flasks were cooled to -78 °C using a dry ice/acetone cold bath. *n*-BuLi (~0.95 equiv) was carefully added dropwise to each flask to ensure that none of the *n*-BuLi was lost on the sides of the flasks. After ~10 min, appropriate increments of HMPA were added to each flask and the run was initiated by careful addition of the neat electrophile (for methyloxirane, 1-chlorobutane, 1-iodobutane or allyl chloride) or a stock solution of the electrophile (for *N*-tosyl-2-methylaziridine). The reactions were run for an appropriate time (15 sec to as much as 15 h, but typically not more than 1 h) to allow initial rate conditions to be maintained (0.1 to 5% reaction, although conversion as high as 30% was unavoidable for the fastest reactions). The reactions were quenched with EtI or MeI (for reaction with epoxide and the halides) or benzaldehyde (for reaction with aziridine) to measure remaining RLi, followed after 10 min by ~2 equiv of an aqueous 1.4 M NH₄Cl solution and dilution with hexane (~2.5 mL). The flasks were then dried with anhydrous Na₂SO₄ and directly analyzed by GC for dodecane, (PhS)₂CH₂, (PhS)₂CH₂Et, and (PhS)₂CH₂Et. The initial and final RLi concentration and product conversion were determined from the average of three GC traces (response factors were determined for all components). Typical mass balance was 90-95%, kinetic points with less than 80% mass balance were discarded.

Reaction orders were determined by series of experiments in which the concentration of either RLi or the electrophile was incremented, typically by a factor of 4-8 in 3-4 steps.

Bis(3,5-bistrifluoromethylphenylthio)methylithium. Carried out as above, except that exceptional care must be taken to avoid local overheating in the preparation of the RLi solution because of the thermal instability of the reagent.

1,3-Dithianyllithium. A 0.5 M stock solution of 1,3-dithianyllithium in THF was prepared by reaction of *n*-BuLi (0.95 equiv) with dithiane at -20 °C for at least 2 h. The stock solution was stored at -78 °C and was not kept longer than 2 days. Solutions for kinetic experiments were prepared by addition of ca 3 mL of a stock solution of dodecane in THF and ca 0.5 mL of the stock solution of 1,3-dithianyllithium to five reaction flasks (including one blank flask to which no HMPA or electrophile was added which was used to determine the concentration of the RLi stock solution). The experiment was then carried out as above.

References Supporting Information

^[S-1] Long-necked flasks (neck ca 7 cm), immersed to a depth of >5 cm from bottom of flask, are required to minimize heat conduction down the flask walls, which results in significant increases in internal temperature if a normal 5 mL round-bottom flask was used.