

Reductive Dimerization of Styrenes Enabled by Flow Microreactors

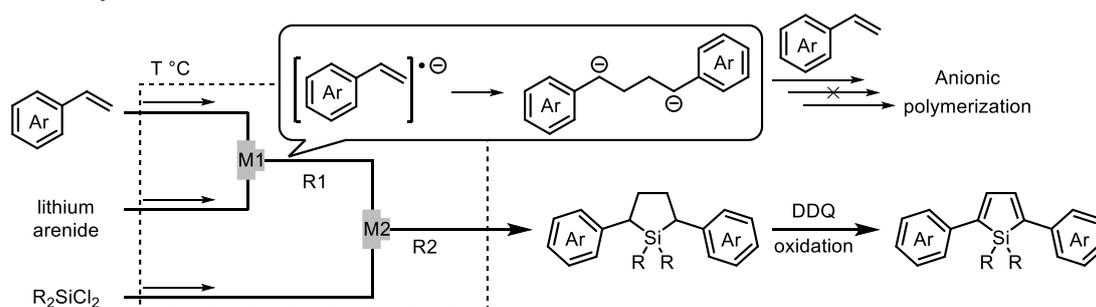
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Although 1,4-dianions are useful precursors to cyclic skeletons, the generation of the dianions is limited to classical methods, such as reduction and halogen-lithium exchange of 1,4-dihaloalkanes. The dimerization of styrene by one-electron reduction can also generate dianions, but the highly reactive dianions easily undergo anionic polymerization.¹

Herein, we report the reaction of styrenes with lithium arenides in a flow microreactor leads to the instantaneous generation of a styryl radical anion and subsequent dimerization yields 1,4-diaryl-1,4-dianions. The efficiency was greatly improved by increasing the flow rate and decreasing the inner diameter of the mixer. Therefore, fast mixing is considered to be essential in this reaction. The efficiency and selectivity of this reductive dimerization was proved to be low in batch-type reactors.

This method is capable of generating the dianions of various styrenes. Furthermore, the generated dianions can react with various electrophiles. Notably, 3,4-unsubstituted 2,5-diarylsiloles can be conveniently synthesized by the reaction of the generated dianion species with dialkyldichlorosilanes followed by oxidation with DDQ. Although siloles have attracted a great deal of attention as a new class of functional materials due to their high electron-accepting and fluorescent properties, the synthetic methods for 3,4-unsubstituted 2,5-diarylsiloles are limited.²



1) M. Szwarc, M. Levy, R. Milkovich, *J. Am. Chem. Soc.* **1956**, 78, 2656.

2) S. Santra, *ChemistrySelect* **2020**, 5, 9034.