

$S_{RN}1$ and Stille Reactions: A New Synthetic Strategy

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Abstract: The photostimulated reaction of Me_3Sn^- ion with mono, di and trichloro arenes in liquid ammonia gave very good yields of stannanes by the $S_{RN}1$ mechanism. These products reacted by a palladium-catalyzed cross coupling reaction with halobenzenes to give phenylated products also in very good yields. Similar yields can be obtained in one-pot reactions.

Introduction

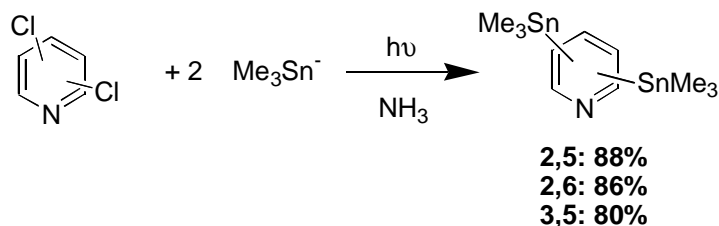
The radical nucleophilic substitution, or $S_{RN}1$ reaction, is a process through which a nucleophilic substitution is obtained [1]. The scope of the process has considerably increased and nowadays it is an important synthetic possibility to achieve substitution of different substrates. Several nucleophiles can be used, such as carbanions and anions from compounds bearing heteroatoms, which react to form new C-C or C-heteroatom bonds in good yields. We thought that the photostimulated reaction of mono-, di- and trichloro- arenes with Me_3Sn^- ions in liquid ammonia to synthesize the trimethylarylstannanes followed by the Pd(0) cross coupling reaction with haloarenes (Stille Reaction) [2,3] would be an important approach for the synthesis of arylated or polyarylated compounds [4]. Thus, we undertook the study of the palladium catalyzed reaction of trimethylarylstannanes, synthesized by the $S_{RN}1$ mechanism, with mono-, di- and trichloro- arenes as a model reaction for this methodology. Also we performed both reactions in one-pot procedures.

Experimental

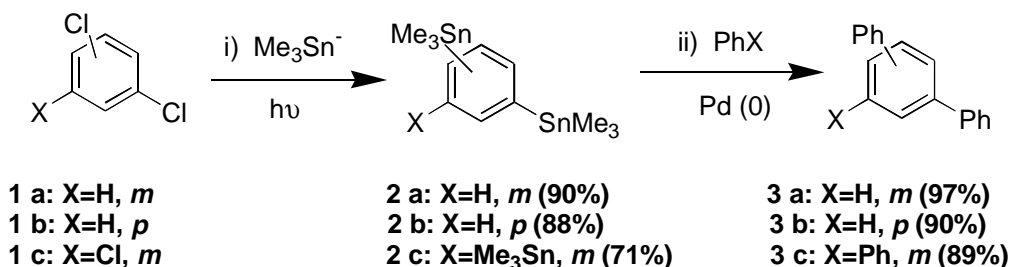
Organotin compounds were obtained by photostimulated reactions in liquid ammonia. Irradiation was conducted in a reactor equipped with two 250-W UV lamps emitting maximally at 350 nm. Cross coupling reactions were carried out with $Pd(PPh_3)_2Cl_2$ as catalyst (3-6%) and DMF as solvent.

Results and Discussion

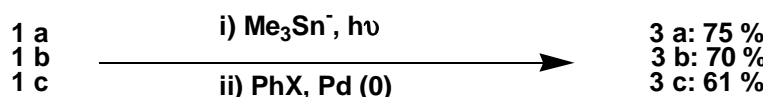
The photostimulated reactions of Me_3Sn^- with dichloropyridines, di- and trichlorobenzenes afford di and tritin compounds in very good yields:



The palladium catalyzed cross coupling reactions of stannanes and aryl halides (PhBr or PhI) gave the respective arylated compounds:



We also studied the possibility of performing the synthesis of the stannane and the Stille reaction in a one-pot procedure:



All these results indicated that the $S_{RN}1$ mechanism is an excellent method to obtain stannanes by the photostimulated reactions of mono-, di- and trichloro arenes with Me_3Sn^- in liquid ammonia. The stannanes thus obtained can be arylated by further reaction with bromo or iodoarenes through the palladium catalyzed reactions (or to perform other palladium-catalyzed reactions). Further work is in progress to examine reactions in a stepwise or one-pot conditions.

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References and Notes

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