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Title: Synthesis of Useful Organic Molecules Involving *N*-thioimides and dithiocarbamates

Abstract:

In this research period, we have synthesized various type of important organic molecules by using *N*-thioimides and dithiocarbamates as substrates. Here, *N*-thioimides molecules have been used as thiolating reagent to produce thiophosphate, thiophosphinate and selenophosphate molecules under neat condition. We have synthesized styrenyl dithiocarbamates and phenacyl-bis(dithiocarbamates) from dithiocarbamate anion under metal free condition. We have developed a unique protocol where dithiocarbamate compounds are used as the carbonyl alternative in carbonylative homocoupling reaction.

A neat reaction protocol has been developed for synthesis of thiophosphate, thiophosphinate and selenophosphate compounds. *N*- thioimides have been used for chalcogenylation of P(O)H moieties of various H-phosphonates under solvent, catalyst and base free condition at room temperature in aerial atmosphere. Both *S*-aryl and *S*-alkyl phosphorothioate compounds were prepared by this method in good yields. Selenophosphates were also synthesized using *N*-(phenylseleno)phthalimide under solvent free condition.

Styrenes have been functionalized to produce styrenyl dithiocarbamates by a one-pot two-step procedure without using any metal catalysts. Styrene was transformed into a bromo-derivative, which undergoes a domino nucleophilic substitution followed by elimination in the presence of a dithiocarbamate anion and triethylamine to produce trans-styrenyl dithiocarbamates exclusively. The reaction shows a wide substrate scope and good yields of products.

The synthesis of phenacyl-bis(dithiocarbamates) has been reported by metal-free trifunctionalization of phenylacetylene systems by following a one-pot two-step strategy. Phenyl acetylene undergoes molecular bromine-mediated oxidative bromination followed by nucleophilic substitution with the freshly prepared dithiocarbamate salt which is prepared by the prompt reaction of amine and CS_2 in the presence of triethylamine base. A series of gem-bis (dithiocarbamates) are prepared using various secondary amines and phenylacetylene systems containing different substituents.

We have developed a novel protocol for carbonylative homocoupling of arylboronic acids using dithiocarbamate ester as the carbonyl alternative. A series of arylboronic acids underwent smooth reaction with dithiocarbamate ester (M_2NCS_2Me) in presence of $Pd(PPh_3)_2Cl_2$ catalyst, $Cu(OAc)_2.H_2O$ additive and Na_2CO_3 in DCE solvent producing the biaryl ketones efficiently. The mechanism has been studied with the help of several control experiments which reveal the probability of thioamide-intermediacy. Chemoselective homocoupling allows the post-synthetic modification of the product.

Manas Mondal 14.11.2024
Signature of candidate

14.11.2024
Signature of supervisor

Dr. Amit Saha
Assistant Professor
Department of Chemistry
Jadavpur University
Kolkata-700032, India