

IN THE NAME OF GOD

NEW APPLICATIONS OF TRIPHENYLPHOSPHINE (PPh₃) AND
ELECTROPHILIC SPECIES IN ORGANIC SYNTHESIS

BY
HAMID REZA SHATERIAN
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EVALUATED AND APPROVED BY THE THESIS COMMITTEE AS:

EXCELLENT

N. Iranpoor

N. Iranpoor, Ph. D., Prof. of Chemistry
(Chairman)

H. Firouzabadi

H. Firouzabadi, Ph. D., Prof. of Chemistry

A. Banihashemi

A. Banihashemi, Ph. D., Prof. of Chemistry

H. Pirelahi

H. Pirelahi, Ph. D., Prof. of Chemistry
(Tehran University)

K. Saidi

K. Saidi, Ph. D., Assoc. Prof. of Chemistry
(Kerman University)

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Dedicated to:

My Father and Mother

and

My Professors:

Professor. M. Jalali & Professor. N. Iranpoor

and

Professor. A. Safavi

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ABSTRACT

NEW APPLICATIONS OF TRIPHENYLPHOSPHINE (PPh₃) AND ELECTROPHILIC SPECIES IN ORGANIC SYNTHESIS

BY

HAMID REZA SHATERIAN

In this study, the preparation of Ph₃P(SCN)₂ was modified by using a combination of Ph₃P, NH₄SCN and Br₂ at room temperature. The one-pot and *in-situ* generation of Ph₃P(SCN)₂ provides an efficient and very simple method for immediate conversion of alcohols, thiols, trialkylsilyl and tetrahydropyranyl ethers to their corresponding thiocyanates in high to excellent yields under mild and neutral reaction conditions. One-pot conversion of carboxylic acids, *tert*-butyldimethylsilyl and *triisopropylsilyl* carboxylates to their corresponding acyl and aroyl isothiocyanates were performed using this reagent. We have also applied this method for preparation of 2-thioxo-3,4-dihydro-2H-1,3-benzoxazine-4-one from salicylic acid or its *triisopropylsilyl* and *tert*-butyldimethylsilyl carboxylates. This compound has fungicidal and bactericidal properties.

Using dithioacetals as source of sulfur compounds, we were able to develop a new and novel method for the reduction of sulfoxides with electrophilic bromine such as N-bromosuccinimide, 2,4,4,6-tetrabromo-2,5-cyclohexadienone and also molecular bromine as catalyst. We have also shown that the use of dimethyl sulfoxide as easily available source of oxygen transfer agent, together with catalytic amounts of electrophilic halogens provides an efficient,

novel and mild procedure for deprotection reactions of cyclic and acyclic dithioacetals and ketals and also 1,3-oxathioacetals.

We also describe a new synthetic method for preparation of dihydro-[1,4]dithiines, dihydro-[1,4]oxathiines, dihydro-5H-[1,4]dithiepins and their chloro, bromo, isothiocyanate derivatives through a ring expansion reaction from 1,3-dithiolanes, 1,3-oxathiolanes and 1,3-dithianes respectively. In addition, a novel synthesis of dihydro-benzo[1,4]dithiines, dihydro-benzo[1,4]oxathiines, dithia-benzocycloheptene and dihydro-naphtho[1,4]dithiine from cyclic S,S- and S,O- ketals of cyclohexanone in the presence of molecular bromine are described. To the best of our knowledge this procedure is the first report in aromatization reaction of cyclic S,S- and S,O- ketals of cyclohexanone.

Deprotection of dithioacetals and oxathioacetals to their corresponding carbonyl compounds with electrophilic halogens on wet silica gel, highly chemoselective acetalization and *in-situ* transacetalization of carbonyl compounds, preparation of diacetals by condensation of carbonyl compounds with 2,2-bis(hydroxymethyl)-1,3-propanol, preparation of acetonides (1,3-dioxolane) from epoxides and also synthesis of 1,1-diacetates from aldehydes, dithioacetalization and oxathioacetalization of carbonyl compounds and transdithioacetalization reactions in the presence of catalytic amounts of compounds carrying electrophilic halogen are described.

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