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**SOLID-PHASE POLYMERIC ANALOGUES OF
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REAGENTS**

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Solid-Phase Polymeric Analogues of Chloramine-T and Bromamine-T: Preparation and Use as Synthetic Reagents

Pushpavathi

Research Scholar, Sai Nath University, Ranchi, Jharkhand

Abstract – Polymeric reagents offer a range of unique advantages. Intramolecular reactions, such as the cyclization of peptides or Dieckmann cyclizations, can be brought about by attaching the reactive molecules at remote points along a polymer chain. In contrast, if the reactive molecules are anchored in close proximity on a polymeric support then intermolecular reactions occur, as demonstrated for a ketone synthesis.

Keywords: Polymeric, Chloramine-T, Bromamine-T, Reagents

INTRODUCTION

The diverse nature of the chemistry of N-halogeno-N-metallo reagents is a consequence of their ability to act as a source of

- (a) Halonium cations,
- (b) Hypohalite species,
- (c) N-anions which act as bases and nucleophiles and
- (d) Nitrenoids in limited cases.

As a result, these reagents react with a surprising range of functional groups affecting an array of molecular transformations¹ Historically the important early developments in the area stemmed from the synthesis of chloramine-T and related aryl sulphonamide derivatives.

Aromatic N-halosulphonamides behave as mild oxidants and halogenating agents containing a strong polarized N-linked halogen which is in +1 state. Bromamine-T (sodium N-bromo-p-toluenesulphonamide or BAT; $\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NBrNa}\cdot 3\text{H}_2\text{O}$) can be easily prepared by bromination of Chloramine-T (CAT) and is found to be a better oxidizing agent than CAT. Literature survey reveals that several works have been carried out with BAT as oxidant. Kinetic study has also been carried out using other oxidant. Tranexamic acid, (TX) [Trans-4-(aminomethyl) cyclohexanecarboxylic acid] is an antifibrinolytic agent and has applications in pharmaceuticals. Its kinetics and oxidation study is

very important. Kinetics and mechanistic study of tranexamic acid by Bromamine-T in alkaline medium catalyzed by Palladium (II) has been studied. Literature survey revealed no information in the kinetics of oxidation of this drug by this oxidant. Hence, kinetics and mechanism of oxidation of tranexamic acid with BAT in HCl medium catalyzed by RuC at 303K have been studied.

REVIEW OF LITERATURE -

Considerable attention has centered on the chemistry of N-haloarenesulphonamides because of their versatile behaviour as mild oxidants, halogenating agents and Nanions. Which act both as bases and nucleophiles. The chlorine compound, chloramine-T (CAT), a by-product in saccharin manufacture, is well-known as an analytical reagent and the mechanistic aspects of its reactions have been documented by Campbell and Johnson¹. Banerji et al. and Gowda and Mahadevappa. The prominent members of this class of compounds are chloramine-T, chloramine-B and the corresponding bromine analogues bromamine-T. Bromamine-B. Since these oxidants react with a wide variety of functional groups, they are used as reagents for analytical and kinetic investigations. Methoxy-benzoyloxybenzyl alcohol (MBBA) resin was synthesized by a two-step sequence under microwave irradiation involving the reaction of commercially available Merrifield [1, 2] resin with vanillin, followed by reduction with sodium borohydride. MBBA resin was treated with bromides in the presence of sodium hydride to afford the corresponding resin-bound benzyl ethers. In the mid-1970s, Hodge [3, 4] used polymer-supported peroxy

acids for the oxidation of olefins, penicillin derivatives and sulphides Both aliphatic and aromatic polymeric peroxy acids have been prepared and used as efficient reagents for the epoxidation of olefins Some extent of selectivity was noticed in the epoxidation of long chain alkenes The periodate form of certain commercially available macroporous anion exchange resins can be used in either protic or aprotic solvents to oxidise various quinols, catechols and glycols.

Titanium reagents are widely used in organic synthesis [5]. Whereas the organotitanium reagents are useful in C-C bond forming reactions, the simple TiX_4 (X = Cl, OR) are frequently used in both stoichiometric and catalytic quantities in C-C bond forming reactions and functional group transformations. Among various titanium reagents, TiCl_4 has vast applications in organic synthesis. It has been used as such or in combination with an additive [7].

In the last 20 years, several useful synthetic transformations involving the use of TiCl_4 along with a tertiary amine NR_3 were uncovered. These results are presented in this account.

The TiCl_4 - NR_3 reagent system has been widely used for the preparation of titanium enolates for applications in aldol and related reactions in organic synthesis. It was first used in Knoevenagel condensation reactions [6].

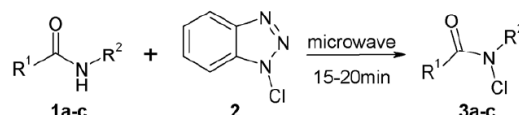
N-CHLORINATION OF AMIDES

N-Haloamides are used as photoinitiators for radical polymerization and in room temperature vulcanization for the preparation of adhesives, caulks and sealants. They are also versatile reagents in organic synthesis as oxidizing agents in aqueous and non-aqueous media; Photolysis of N-haloamides gives amidyl radicals and halogen atom intermediates. The amidyl radicals so produced undergo efficient intramolecular addition to olefinic bonds. Olefinic amidyl radicals can ring-close to lactams or N-heterocyclic amides. N-chloroamides undergo the Hofmann reaction and Orton rearrangements.

Many literature methods are reported for the synthesis of primary N-chloroamides. Routes to synthesize secondary N-chloroamides include chlorination of secondary amides with NaCl in the presence of oxone, t-butyl hypochlorite, sodium hypochlorite, and N-chlorosuccinimide these methods for the synthesis of secondary N-chloroamides have their own limitations. t-Butyl hypochlorite is unstable and hazardous, reaction with NaCl in presence of oxone can require 2-5 hours Microwave heating has emerged as an environmental friendly technique to accelerate a variety of chemical reactions Automated and focused microwave flash heating has recently been demonstrated to improve the preparative efficacy and to dramatically reduce reaction times

for many different types of organic transformations. We now report that by applying microwave heating, the N-chlorination of cyclic and acyclic secondary amides can be done in 15-20 minutes using N-chlorobenzotriazole as the chlorinating agent.

Optimization of the reaction conditions was carried out for the chlorination of secondary amides and different combinations of temperature, time and irradiation power were studied for N-methylbenzamide (1a) in order to achieve the maximum chemical yield at the lowest reaction temperature. Microwave irradiation of 1a for more than 20 minutes caused decomposition.



Scheme: Synthesis of secondary N-chloramines

	R^1	R^2	Time (min)	Temp ($^{\circ}\text{C}$)	Power (Watts)	Yield (%)	Lit. yield (%)
3a	$-\text{C}_6\text{H}_5$	$-\text{CH}_3$	15	65	80	80	85 ³² 98 ³³
3b	$-\text{C}_6\text{H}_5$	$-\text{CH}_2\text{C}_6\text{H}_5$	15	65	90	82	-
3c	$-\text{CH}_3$	$-\text{C}_3\text{H}_7$	20	50	80	87	71 ³⁴

Table: Microwave Conditions and yields for the preparation of secondary N-chloroamides

CONCLUSION:

In this paper we found that the synthesis of N-chloro-N-methylbenzamide reported with t-butylhypochlorite in high yields but requires 12 hour reaction conditions are mild and the reaction can be finished in 15 minutes time. The same methodology converted cyclic secondary amides into the corresponding N-chloro amides in good to excellent yields in 15 minutes. The benzotriazole formed in the reactions removed by washing with a saturated solution of sodium carbonate to give pure products.

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