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A simple and efficient bromoformyloxylation and bromoacetoxylation reaction using $TsNBr_2$

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ABSTRACT

Bromoformyloxylation and bromoacetoxylation of olefins proceed smoothly and instantaneously in the presence of *N,N*-dibromo-*p*-toluene sulfonamide without any catalyst. The one step reactions can be carried out with all kinds of olefins in high yield and high regio and stereoselectivities.

The vicinal functionalization of alkenes is an important process in synthetic organic chemistry. Among the several methodologies found in the literature,[1] halofunctionalization[2] of alkenes toward synthetically useful substrates attract much more attention. Such type of reactions, also termed as 'cohalogenation' uses a combination of positive halogen source and appropriate nucleophile sources such as water, alcohols, or acids.[3] These reactions are attractive tools to produce vicinal halo-functionalized compounds regioselectively, which are useful intermediates for diverse organic transformations. For example, chloroformyloxylation of olefins is synthetically useful in order to obtain bifunctionalities with regioselectivity.[4]

Literature study reveals that limited attempts have been made to explore this particular type of reaction. Using Vilsmeier reagent, Ziegenbein et al. synthesised chloroformyloxylated product from epoxides.[5] Kim et al. synthesised chloroformylloxylated product using HCl and DMF in the presence of an oxidant such as *m*-CPBA or oxone.[6] This procedure requires HCl gas in DMF besides hazardous *m*-CPBA. *N*-halosuccinimides have also been used as halogen source for such type of reactions.[7] This reagent produces low yields of the desired product after long reaction hours. Takemura studied bromoformyloxylation using *N,N*-dibromobenzene sulfonamide in the presence of 99% formic acid in chloroform at low temperarure.[8] This reaction was found to be very slow in case of α,β unsaturated esters, which produces low yields of the product after several hours of reaction. *N*-Bromosaccharin (*N*BSac) has been successfully utilized by de Mattos for bromoformyloxylation of simple alkenes.[9] However, efficacy of this reagent was not tested for other alkenes such as cinnamates and chalcones. Trichloroisocyanuric acid (TCCA),[9,10] I_2/Fe(III) salts[9,11] were also used by the same group for the synthesis of other haloformates.

Another cohalogenation reaction is the bromoacetoxylation reaction where vicinal bromo acetoxy products are synthesized. This reaction also received scant attention in the literature. de Almeida et al. synthesised some compounds using tribromoisocyanuric acid as the brominating agent.[12] Yeung and co-workers used NBS for bromoacetoxylation reaction in the presence of molecular sieves as catalysts.[13] A number of limitations such as long reaction time, requirement of dark conditions, and high catalyst loading make this procedure inconvenient. Using NaBr as bromine source, Pandit isolated a few bromoacetoxylated products in the presence of $PhI(OAc)_2$ as oxidant in the presence of CTAB in DCM.[14] Negoro found that, vicinal bromo actoxy product forms in low yields in a reaction of styrene with tetrabutyl ammonium dichlorobromate in acetic acid.[15] Other methods such as haloesterification of diols[16] and acetylation of corresponding vicinal halohydrins[17] were also reported. However, these methods require the synthesis of precursor diols or halohydrins from corresponding olefins.

We sought to develop a procedure for cohalogenation reaction which is simple and trouble-free and can provide a better yield in a shorter time period. In continuation of our investigations on various organic transformations using *N,N*-dibromo-*p*-toluenesulfonamide ($TsNBr_2$),[18] we report herein the synthesis of formyloxy bromides and acetyloxy bromides (Scheme 1).

To begin with, a study was carried out with styrene as a model substrate. A reaction was carried out by adding $TsNBr_2$ to the solution of styrene in DMF. The whole process was carried out at

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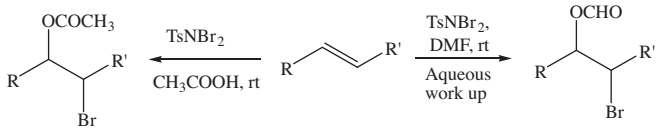


Scheme 1. Cohalogenation reaction using $TsNBr_2$.

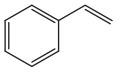
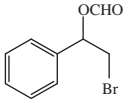
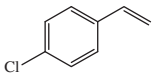
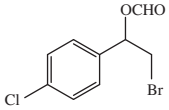
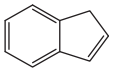
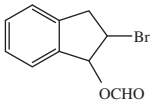
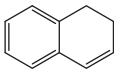
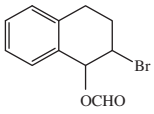
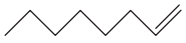
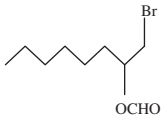
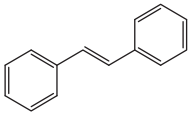
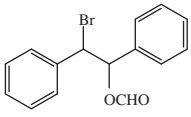
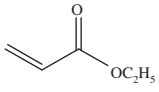
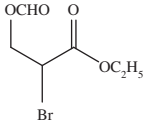
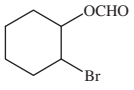
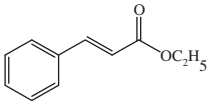
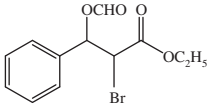
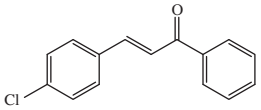
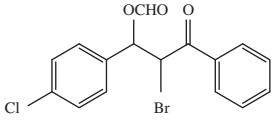
room temperature under nitrogen atmosphere. The reaction was studied by using 1 equiv of $TsNBr_2$ (based on the olefinic substrate). We observed that after addition; the olefin disappears instantaneously in an exothermic process, which was confirmed by monitoring the reaction by TLC. The reaction mixture was stirred for another 10 min. After usual aqueous work-up, and chromatographic purification, corresponding formyloxy bromide was obtained in an 85% yield. When the reaction was further examined using 0.5 equiv of $TsNBr_2$ the corresponding product was obtained in 63% yields. Hence equimolar amount of $TsNBr_2$ (based on the substrate) was considered to be optimum for the reaction.

This process was extended to a variety of olefins.[19] The reaction was carried out using 1 mmol of olefin, 1 mmol of $TsNBr_2$ in DMF (2 mL) at room temperature followed by aqueous work-up. Results are summarized in Table 1.

From Table 1 it is seen that not only the styrenes but also the aliphatic olefins react very smoothly to give the corresponding formyloxy bromides. Usually the α,β unsaturated compounds are not so reactive species. In our case, cinnamate, chalcone as well as acrylates also gave encouraging results. From the NMR study, it was confirmed that the reaction was highly regio and stereoselective.

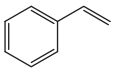
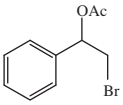
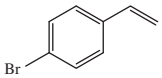
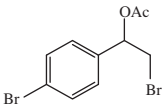
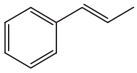
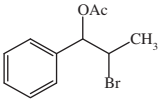
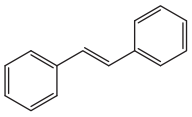
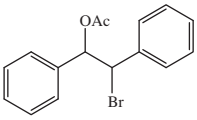
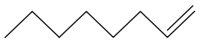
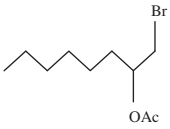
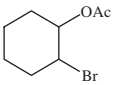
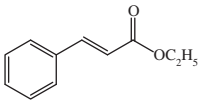
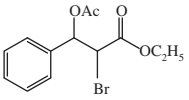
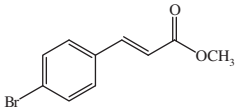
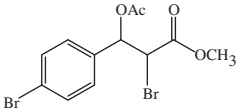
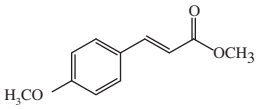
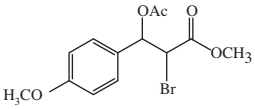
After successful isolation of the formyloxy bromides, we changed the solvent of the model reaction, from DMF to acetic acid, using styrene as substrate under the same reaction condition.[19] We found pronounced effect on changing the media, where OAc group is transferred along with the bromine and acetyloxy bromide was isolated. We observed that the reaction produces the

Table 1
Bromoformyloxylation reaction using $TsNBr_2$

Sl. No.	Substrate	Product	Yeild[a]	Ref.
1			85	8
2			84	–
3			79	–
4			78	–
5			86	8,9
6			80	–
7			86	–
8			88	8,9
9			91	8
10			85	–

[a] isolated yield after chromatographic purification.

Table 2
Bromoacetoxylation reaction using $TsNBr_2$

Sl. No.	Substrate	Product	Yield[a]	Ref.
11			88	13
12			78	17a
13			95	15
14			76	13
15			75	16
16			76	13
17			86	14
18			80	–
19			82	17b

[a] Isolated yield after chromatographic purification.

corresponding bromo acetyloxy products instantaneously. After initial success, attempts were made taking other olefins as substrates and we were able to isolate different acetyloxy bromides in excellent yields. Results are summarized in Table 2. In this case also the reaction was found to be regio- and stereoselective.

In summary, we have developed a very efficient, quick, and simple procedure for the bromoformyloxylation as well as bromoacetoxylation of olefins. The procedure produces formyloxy bromides and acetyloxy bromides instantaneously from olefins. All kinds of olefins such as styrene, cinnamate, acrylate, chalcone, aliphatic olefin etc. produce corresponding cohalogenated products in excellent yields.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.11.138.

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19. *Experimental procedure*: To a solution of olefin (1 mmol) in 2 mL of DMF (or acetic acid), $TsNBr_2$ (1 mmol) was added under nitrogen atmosphere and stirred. After 10 min of reaction, sodium thiosulfate (200 mg approx.) was added followed by the addition of water (5 mL). The reaction mixture was stirred for 15 min and taken up in ethyl acetate. Organic layer was separated, washed with brine (saturated sodium bicarbonate solution and brine for Bromoacetoxylation), and dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by flash chromatography on silica gel (230–400 mesh) with petroleum ether/ethyl acetate as eluent.