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Facile generation of *vicinal* bromoazides from olefins using $TMSN_3$ and $TsNBr_2$ without any catalyst

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ABSTRACT

A very rapid and efficient method has been developed for the synthesis of *vicinal* bromoazides directly from olefin using *N*,*N*-dibromo-*p*-toluenesulfonamide ($TsNBr_2$) without any catalyst. The reaction is extremely fast which goes into completion instantaneously to produce bromoazides. This procedure is applicable to various olefins such as cinnamates, chalcone, styrenes, and acrylate to give the corresponding 1,2-bromoazide in an excellent yield.

Organic azides are versatile building blocks with a diverse range of applications in organic chemistry,[1] with a use as intermediates for the construction of synthetically and biologically important compounds such as amines[2] and heterocycles.[3] In recent past, azido compounds have also been gaining importance as the key intermediates in the emerging field of 'click chemistry'.[4] Haloazidation is an important organic transformation for simultaneous introduction of halogen and azide functionality onto an olefin. The resulting haloazides can be subjected to further synthetic manipulations to achieve a variety of compounds such as vinyl azide,[5] amines,[6] aziridins,[7] and tetrazoles.[8] Vicinal iodoazidation is known in the literature for a long time. Hantsch reported for the first time in 1900 a strategy for the synthesis of 1,2-iodoazides using silver azide and iodine in ether.[9] 1,2-Iodoazides can also be synthesized by treating ICl/NaN_3,[10] $PhI(OAc)_2/Et_4NX/TMSN_3$,[11] $CAN/NaI/NaN_3$,[12] $IPy_2BF_4/TMSN_3$,[13] and Oxone/wet $Al_2O_3/KI/NaN_3$[14] with alkenes under various conditions. Poor selectivity and instability of these iodoazides are the main problems of these methods. Later, Hassner developed a procedure for *vic*-bromoazidation of alkene by addition of bromine azide generated from bromine and sodium azide.[15] This procedure requires the use of excess hydrazoic acid to suppress the formation of dibromo compounds. A similar procedure was also reported by Krief for bromoazidation of alkenes by bromine azide which was generated in situ from NBS and NaN_3.[16] Olah employed NBS and $TMSN_3$ for the bromoazidation of alkenes in the presence of Nafion-H in DME/H_2O.[17] However this procedure was reported only for 1,2-disubstituted and trisubstituted alkenes and there was no reaction with terminal alkenes. Recently, Hajra et al reported a method for 1,2-bromoazidation of alkenes using NBS and $TMSN_3$ in the presence of $Zn(OTf)_2$ catalyst,[18,19] however, metal triflates are highly expensive. Although, this method works well with terminal and 1,2-disubstituted olefins, α,β-unsaturated carbonyl compounds take much longer time and require higher temperature to achieve a good yield. Moreover, for chalcone, the reaction does not go into completion even after a long reaction time at a high temperature with a poor yield. Bromoazidation with α,β-unsaturated carboxylic acid derivatives also takes much longer time even at a higher temperature.[19]Therefore, the development of efficient methods for *vicinal* bromoazidation of alkenes, particularly in the case of α,β-unsaturated alkenes, remains a challenging task. We are reporting herein a rapid and efficient procedure for the vicinal bromoazidation of alkenes using *N*,*N*-dibromo-*p*-toluene sulfonamide ($TsNBr_2$) as bromine source and $TMSN_3$ as azide source (Scheme 1). This reaction works well with all kinds of alkenes including α,β-unsaturated carbonyl compounds at room temperature within a very short time, without any catalyst.

N,*N*-Dibromo-*p*-toluenesulfonamide is known for a long time for aminobromination reaction in organic synthesis. Since the discovery of this reagent by Kharasc,[20] it has been utilized for

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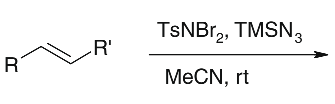


R = Aryl, H
R' = Aryl, alkyl, COR, COOR

Scheme 1.

Table 1
Synthesis of bromoazides in different solvents

Entry	Solvent	Yield (%)
1	CH_3CN	76
2	CH_2Cl_2	76
3	Toluene	58
4	CCl_4	61
5	DMF	58
6	Acetone	39

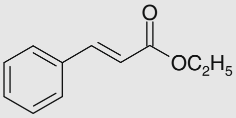
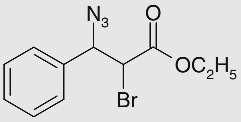
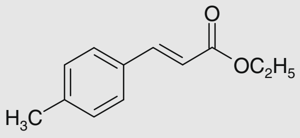
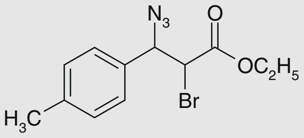
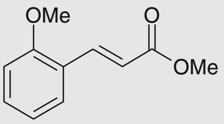
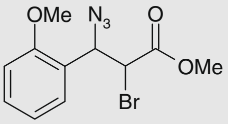
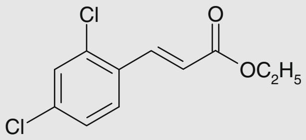
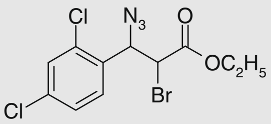
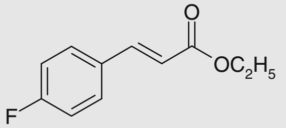
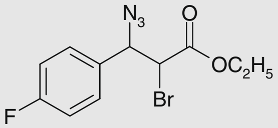
Reaction conditions: olefin (1 mmol), $TMSN_3$ (1.1 mmol), $TsNBr_2$ (1.2 mmol), solvent (2 mL), rt, 10 min.

aminobromination of a variety of olefinic substrates.[21] Recently, we have also developed a method for the synthesis of bromohydrins and alkoxy bromides using $TsNBr_2$.[22] The brominating agent $TsNBr_2$ employed for this purpose was prepared from Chloramine-T by following literature procedure.[23]

To begin with, a study on the bromoazidation reaction was carried out with ethyl cinnamate as a model substrate. The reaction was carried out by adding $TMSN_3$ to the solution of ethylcinnamate in acetonitrile followed by the addition of $TsNBr_2$. The whole process was carried out at room temperature under nitrogen atmosphere. The reaction was studied by using 1.1 equiv of $TMSN_3$ (based on the olefinic substrate) and 1.2 equiv of $TsNBr_2$. We observed that after addition, the olefin disappears instantaneously, which was confirmed by monitoring the reaction by TLC. The reaction mixture was stirred for another 10 min. After usual work-up the corresponding bromoazide was obtained in an excellent yield. The reaction was further studied using different solvents such as dichloromethane, toluene, carbon tetrachloride, dimethylformamide, and acetone under the same reaction conditions (Table 1). Both acetonitrile and dichloromethane gave similar results for the azidobromination reaction. However, use of other solvents such as toluene, carbon tetrachloride, DMF, and acetone was not fruitful (Table 1).

The reagent is much faster than NBS for bromoazidation reaction. Secondly, for NBS-assisted bromoazidation reaction, it is necessary to add a suitable catalyst to promote the reaction.[17,18] But, in this case, reaction goes into completion without any catalyst. This process was extended to a variety of olefins in acetonitrile as solvent. The results are summarized in Table 2. Initially, we examined the reaction for different cinnamic esters. It can be seen from Table 2 that various cinnamic esters bearing functional groups such as $–CH_3$, –OMe, –Cl, and –F reacted successfully to give the corresponding 1,2-bromoazide in high yields irrespective of the substituent position on the aromatic ring.[24] Cinnamic esters having both electron-withdrawing and electron-donating groups could also be converted to the corresponding products in high yields. The reaction is regioselective, however, moderate stereoselectivity

Table 2
Bromoazidation of various alkenes with $TsNBr_2$ and $TMSN_3$[a]

Entry	Alkene (a)	Product (b)	Yield[b]	*anti/syn* ratio[c]
1			76	70:30
2			78	73:27
3			85	64:36
4			86	56:44
5			83	nd