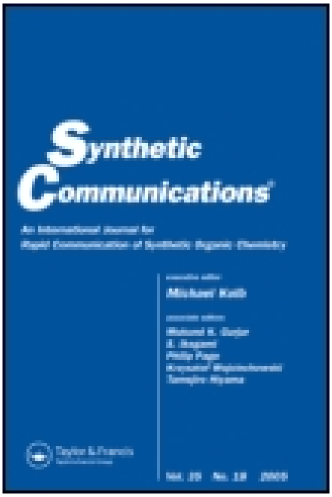

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An Unusual Copper Catalyzed Iodine Mediated Aziridination of Olefins with the Direct Use of *p*-Toluenesulphonamide

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Abstract: *p*-Toluenesulphonamide/I_2 was found to be an efficient system for the copper catalyzed aziridination of olefins in good yields under very mild conditions.

Keywords: Aziridination, copper, iodine, olefins, *p*-toluenesulphonamide

Aziridination of alkenes is an important synthetic transformation as aziridines find broad utility as electrophiles[1,2] and as synthetic intermediates in the preparation of pharmaceuticals and agrochemicals.[3,4] Although the formation of aziridines from the addition of thermally or photochemically generated nitrenes to olefins is a well-known reaction, its utility is limited due to low yields and competing hydrogen abstraction and insertion reactions.[5–7] Metal catalyzed reactions of in situ-generated nitrenes with olefins are an efficient and practical method for the preparation of aziridines and have received increasing attention in recent years. In this context [*N*-(*p*-tolylsulphonyl) imino] phenyliodinane (PhI=NTs)[8] has been widely used as a nitrene precursor for the aziridination of alkenes in the presence of several transition metal-based catalysts.[9–13]

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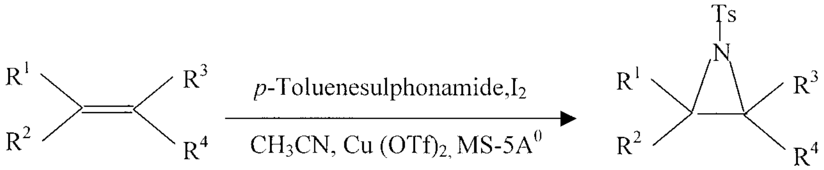


Scheme 1.

However, there are drawbacks with the use of PhI=NTs as a nitrene precursor, it is difficult to prepare and isolate, expensive, yields iodobenzene in equimolar amounts, and oxygenated hydrocarbons are dominent by-products.[14]

In recent years *N*-halo-*N*-metallo salts of sulphonamides such as Chloramine-T and Bromamine-T have been used as a cheap, convenient, and practical nitrogen source for aziridination of alkenes,[15–20] but the methods suffer from certain drawbacks such as the lower yields of the products due to competing hydrogen abstraction and insertion reactions and the formation of *p*-toluenesulphonamide as the side product.

The direct use of sulphonamides as nitrene precursors for the transition metal catalyzed aziridination of olefins is a desirable goal from a synthetic point of view. In this letter we report for the first time an unusual and highly efficient copper catalyzed aziridination of olefins with *p*-toluenesulphonamide in the presence of iodine (Scheme 1). The aziridination of a variety of alkenes was achieved under very mild conditions by reacting alkene (1 eq.) with *p*-toluenesulphonamide (1.2 eq.) and iodine (1.2 eq.) using catalytic amount of Cu (II) triflate (5 mol%) in presence of MS-5A^0 in acetonitrile at ambient temperature under nitrogen atmosphere[1]. These results are presented in Table 1. In these experiments yields of the products are comparable to those

[1] *Typical experimental procedure*: To a stirred mixture of Cu $(OTf)_2$ (18 mg, 5 mol%) and 4-methylstyrene (118 mg, 1 mmol) in acetonitrile (5 mL) was added *p*-toluenesulphonamide (205 mg, 1.2 mmol), iodine (303 mg, 1.2 mmol) and powdered 5Å molecular sieves (100 mg) under a nitrogen atmosphere at 25°C. Stirring was further continued for 3.5 h. The reaction progress was monitored by TLC (SiO_2) using ethylacetate/hexane (4 : 6) as solvent system. After completion, solvent was evaporated under reduced pressure. The residue obtained was purified by passing through a short silica gel column using hexane/ethyl acetate (4 : 6) as eluent. Evaporation of the solvent yielded *N*-(*p*-tolylsulphonyl)-2-(*p*-methylphenyl)aziridine (Yield 230 mg, 80%). IR ν_{max} (cm^{-1}) 3034, 1600, 1516, 1360, 1158; ^{1}H NMR (δ ppm) 2.30 (s, 3H), 2.36 (d, J = 4.2 Hz, 1H), 2.42 (s, 3H), 2.96 (d, 7.16 Hz, 1H)), 3.73 (dd, 7.16, 4.2 Hz, 1H), 7.33–7.09 (m, 6H), 7.87 (d, 2H). Similarly other aziridines were prepared.

Table 1. Copper catalyzed aziridination of olefins with *p*-toluenesulphonamide*

Entry	Olefin	Reaction time (h)	Yield[a] (%)
1	Styrene	5.0	70
2	4-Methylstyrene	3.5	80
3	3-Methylstyrene	4.0	75
4	α -Methylstyrene	2.0	85
5	Methylmethacrylate	6.5	60
6	Cycloheptene	8.0	50
7	Vinylcyclohexane	5.5	55
8	*Trans*-methylcinnamate	12.0	45
9	4-Chlorostyrene	8.0	60
10	Cyclohexene	5.0	55

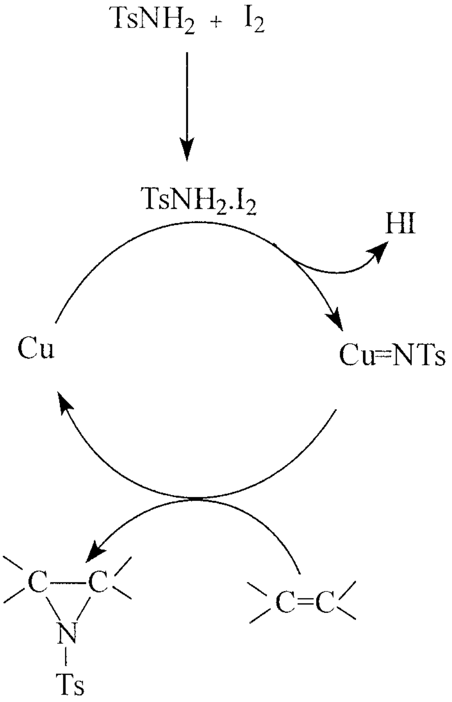
[a]Isolated yield.

*Reaction conditions: Cu $(OTf)_2$ (5 mol%), substrate (1.0 mmol), *p*-toluenesulphonamide (1.2 mmol), Iodine (1.2 mmol) acetonitrile (5 mL), 25°C, 3.5 h, in presence of 5Å molecular sieves under N_2 atmosphere.

obtained in the aziridinations using [*N*-(*p*-tolylsulphonyl)imino] phenyliodinane (PhI=NTs) as the nitrene precursor. In general aromatic substituted alkenes afforded better yields of aziridines compared to aliphatic alkenes. Furthermore, aromatic substituted alkenes bearing electron-donating groups on the benzene ring were found to be more reactive.

To evaluate the effect of catalyst, blank experiment was carried out using 4-methylstyrene as the substrate under similar reaction conditions. In the absence of catalyst intricate mixture of the products was formed. In order to examine the efficiency of various copper catalysts, the aziridination of 4-methylstyrene was carried out using different copper complexes such as $Cu(OTf)_2$, $Cu(acac)_2$, CuCl, $CuCl_2$ as catalysts under similar reaction conditions. Among the various catalysts studied, $Cu(OTf)_2$ was found to be the most efficient catalyst for this transformation. The presence of iodine was found to be essential and the reaction did not proceed in the absence of iodine. A detailed mechanistic speculation of this reaction is premature at this stage. The formation of iodoamine complexes by the reaction of amines with iodine is reported in the literature.[21–23] We assumed that such iodoamine complex formed from *p*-toluenesulphonamide and iodine yield nitroid species, Cu=NTs in the presence of catalyst, which is capable of transferring nitrene to alkenes to yield aziridines (Schemes 1 and 2).

In summary, the present method describes for the first time the direct use of *p*-toluenesulphonamide for the copper catalyzed aziridination of olefins in the presence of iodine.



Scheme 2.

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