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Aziridination of alkenes using *N*-iodo-*N*-potassio-*p*-toluenesulphonamide as a nitrene precursor

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Abstract—N-Iodo-N-potassio-p-toluenesulphonamide was found to be a convenient nitrene precursor for the aziridination of alkenes in the presence of copper catalysts. © 2002 Elsevier Science Ltd. All rights reserved.

Aziridination of alkenes is an important synthetic transformation as aziridines find broad utility as electrophiles¹ and as synthetic intermediates in the preparation of pharmaceuticals and agrochemicals.² 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.³ Metal catalyzed reactions of in situ generated nitrenes with olefins is an efficient and practical method for the preparation of aziridines and has received increasing attention in recent years. In this [N-(p-tolylsulphonyl)imino]phenyliodinane context $(PhI = NTs)^4$ has been widely used as a nitrene precursor for the aziridination of alkenes in the presence of several transition metal based catalysts.⁵

However, there are drawbacks with the use of PhI = NTs as a nitrene precursor,⁶ it is expensive, yields iodobenzene in equimolar amounts and oxygenated hydrocarbons are dominant by-products. Several litera-

ture reports⁷ have described the use of chloramine-T (*N*-chloro-*N*-sodio-*p*-toluenesulphonamide) as a cheap and convenient nitrene source for the aziridination of alkenes, however, yields obtained in general remain moderate to poor and less than those obtained using PhI = NTs. Recently Chanda et al.⁸ reported that bromamine-T (*N*-bromo-*N*-sodio-*p*-toluenesulphonamide) is a superior source of nitrene for the aziridination of alkenes. In continuation of our studies on transition metal catalyzed synthetic transformations,⁹ herein we report copper-catalyzed aziridination of olefins in moderate to high yields using *N*-iodo-*N*-potassio-*p*-toluene-sulphonamide (TsN·KI)¹⁰ as the nitrene precursor (Scheme 1).

The reaction was generalized by reacting a variety of alkenes with N-iodo-N-potassio-p-toluenesulphonamide using CuCl as catalyst.¹¹ The results are presented in Table 1 and indicated clearly that aromatic substituted alkenes afforded better yields of aziridines as compared to aliphatic alkenes. Furthermore, aro-



Scheme 1.

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Table 1. Cuprous chloride-catalyzed aziridination of olefins using *N*-iodo-*N*-potassio-*p*-toluenesulphonamide as nitrene precursor^a

Entry	Olefin	Yield ^b (%)	
1	Styrene	50	
2	4-Methylstyrene	75	
3	3-Methylstyrene	70	
4	α-Methylstyrene	80	
5	Methylmethacrylate	48	
6	Cycloheptene	55	
7	Vinylcyclohexane	52	
8	Norbornene	55	
9	4-Chlorostyrene	60	
10	Cyclooctene	40	

^a Reaction conditions: CuCl (5 mol%), substrate (2.5 mmol), *N*-iodo-*N*-potassio-*p*-toluenesulphonamide (0.5 mmol) acetonitrile (5 ml) in the presence of 5 Å molecular sieves under a N_2 atmosphere at 25°C, 3 h.

^b Isolated yields.

Table 2. Copper catalyzed aziridination of 4-methylstyrene using N-iodo-N-potassio-p-toluenesulphonamide as nitrene precursor^a

Entry	Substrate	Catalyst	Additive	Yield ^b (%)
1 2 3 4 5	4-Methylstyrene 4-Methylstyrene 4-Methylstyrene 4-Methylstyrene 4-Methylstyrene	Cu(I)Cl Cu(I)Cl CuCl ₂ Cu(OTf) ₂ Cu(acac) ₂	5 Å MS 5 Å MS 5 Å MS 5 Å MS	50 75 70 80 80

^a Reaction conditions: catalyst (5 mol%), 4-methylstyrene (2.5 mmol), *N*-iodo-*N*-potassio-*p*-toluenesulphonamide (0.5 mmol) acetonitrile (5 ml), 25°C, 3 h under a N_2 atmosphere.

^b Isolated yields.

matic substituted alkenes bearing electron-donating groups on the benzene ring were found to be more reactive (Table 1, entries 2, 3, and 4). To evaluate the efficiency of various copper catalysts, the reaction of 4-methylstyrene with *N*-iodo-*N*-potassio-*p*-toluene-sulphonamide was studied using different copper complexes as catalysts and acetonitrile as the solvent, with a substrate/*N*-iodo-*N*-potassio-*p*-toluenesulphonamide ratio of 5:1 in the presence of molecular sieves. The results are summarized in Table 2. Cu(OTf)₂ and Cu(acac)₂ were found to be better catalysts in comparison to the other copper salts investigated.

To compare the efficiency of *N*-iodo-*N*-potassio-*p*-toluenesulphonamide with chloramine-T and bro-

mamine-T as nitrene precursors for aziridination reactions, their reactions with 4-methylstyrene were carried out under similar conditions using CuCl as catalyst. The results are presented in Table 3 and show that N-iodo-N-potassio-p-toluenesulphonamide is a superior nitrene source as compared to chloramine-T and bromamine-T for the aziridination of alkenes. The enhanced reactivity of N-iodo-N-potassio-p-toluenesulphonamide may be due to the weak bonding between the nitrogen and the iodine which facilitates the formation of a copper-nitrenoid complex. All these reactions were associated with the formation of *p*-toluenesulphonamide as a by-product along with the aziridine and reactions conducted without the use of 5 A molecular sieves showed significant increase in ptoluenesulphonamide formation.

In summary, the paper describes the use of N-iodo-N-potassio-p-toluenesulphonamide (TsN·KI) as a convenient nitrene precursor for copper catalyzed aziridination of alkenes for the first time. The simple and cost effective preparation of N-iodo-N-potassio-p-toluenesulphonamide (TsN·KI) and better yields of aziridines as compared to those obtained using chloramine-T and bromamine-T make this procedure useful and attractive for aziridination of a variety of alkenes.

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Table 3. Comparison of cuprous chloride-catalyzed aziridination of 4-methylstyrene with different nitrene precursors^a

Entry	Substrate	Nitrene donor	Yield ^b (%)
1	4-Methylstyrene	Chloramine-T	45
2	4-Methylstyrene	Bromamine-T	60
3	4-Methylstyrene	N-Iodo-N-potassio-p-toluenesulphonamide	75

^a Reaction conditions: CuCl (5 mol%), 4-methylstyrene (2.5 mmol), nitrene donor (0.5 mmol), acetonitrile (5 ml), 25°C, 3 h, in the presence of 5 Å molecular sieves under a N₂ atmosphere.

^b Isolated yields.

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- 10. Preparation of *N*-iodo-*N*-potassio-*p*-toluenesulphonamide: *p*-toluenesulphonamide (10 mmol) was dissolved in KOH (20 mmol) in a minimum amount of water. The resulting solution was treated with iodine (20 mmol) at room temperature. Precipitated *N*-iodo-*N*-potassio-*p*toluenesulphonamide was filtered on a Buckner funnel and recrystallized with water. *N*-Iodo-*N*-potassio-*p*toluenesulphonamide thus obtained was dried under vacuum at 100°C and could be stored in a dessicator over calcium chloride for a long period without any decomposition. {E. Viel. Fr. 1950, 957,036. (CA, 46:9599h)}.
- 11. Typical experimental procedure: To a stirred mixture of CuCl (2.5 mg, 5 mol%) and 4-methylstyrene (295 mg, 2.5 mmol) in acetonitrile (5 ml) was added anhydrous *N*-iodo-*N*-potassio-*p*-toluenesulphonamide (167 mg, 0.5 mmol) and powdered 5 Å molecular sieves (100 mg) under a nitrogen atmosphere at 25°C. Stirring was further continued for 3 h followed by filtration on a Buchner funnel. The reaction mixture was then passed through a small silica gel column using ethyl acetate as eluent. Evaporation of the solvent yielded an oil which was purified by column chromatography (silica gel) using hexane/ethyl acetate (4:1) as eluent. Evaporation of the solvent yielded *N*-(*p*-tolylsulphonyl)-2-(*p*-methylphenyl)-aziridine (yield 216 mg, 75%). Similarly other aziridines were prepared.