Investigations in the Transition Metal Catalyzed Aziridination of Olefins, Amination, and Other Insertion Reactions with Bromamine-T as the Source of Nitrene†

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Investigations into the transition metal catalyzed aziridination of olefins with Bromamine-T as a new source of nitrene is presented in this account. Comparison of Chloramine-T and Bromamine-T in this reaction indicates that the latter is superior as the source of nitrene. Systematic study with several transition metal based catalysts suggests that Cu-halides are the best catalysts. A first report of aziridination under microwave and ultrasound irradiation conditions is also presented. Copper-catalyzed aziridination of methyl cinnamate with Bromamine-T did not proceed at ambient temperature but was effected smoothly under ultrasound irradiation to furnish *trans*-aziridine selectively, while under microwave irradiation, a mixture of cis and trans isomers. was obtained. It has been demonstrated that aziridination of olefins proceeds smoothly with inexpensive bleaching powder. Preliminary results of Rh-catalyzed benzylic insertion reactions with Bromamine-T are included in this account.

Introduction

Aziridines, belonging to the group of the smallest of heterocycles, are an important class of compounds in organic chemistry.[1] Significance of this nitrogen-containing heterocycle is due to its presence as a subunit in several natural products,[1b] as efficient chiral auxiliaries[1b] and as ligands in metal-catalyzed asymmetric transformations.[2] Owing to their varied applications, synthesis of aziridines is a subject of considerable research over several years.

A single atom transfer to olefins is the shortest route to three-membered cyclic compounds. This mode is extensively explored for the preparation of cyclopropanes[3a] and epoxides[3b] from olefins. Catalytic addition of a carbene moiety to imine results in the formation of aziridine, but the yields are often on lower side.[4] Similarly, the transfer of a nitrogen atom onto an olefin offers an attractive synthesis of aziridine. Thermally or photochemically generated nitrenes are known to react with olefins to form aziridines; however, their utility is limited due to poor conversions and formation of side products.[5]

The metal-catalyzed reaction of in situ generated nitrenes with olefins is an efficient method for the practical preparation of aziridines and has received much attention in recent years. The first metal-catalyzed nitrogen atom transfer process was reported by Kwart and Khan[6] who demonstrated the decomposition of benzenesulfonyl azide when heated in copper dust in the presence of cyclohexene resulting in the formation of the corresponding aziridine (Scheme 1).

A popular approach to prepare aziridines is via the reaction of nitrene generated from [*N*-(arenesulfonyl)-imino]phenyliodinanes[7,8] ($PhI{=}NSO_2Ar$) with olefins. Several transition metal based catalysts are employed for the acceleration of this reaction via the intermediate metal nitrenoid species. In another approach aziridine-2-carboxylates are prepared by reaction of (ethoxycarbonyl)nitrene generated from ethyl *N*-[(4-nitrobenzenesulfonyl)oxy]carbamate ($NsONHCO_2Et$).[9] Recently, Chloramine-T (TsNNaCl) has been introduced[10a] as a source of nitrogen in the copper(I)-catalyzed aziridination of olefins.

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† This paper is dedicated to Dr. T. Ravindranathan on the occasion of his 60th birthday.

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Scheme 1

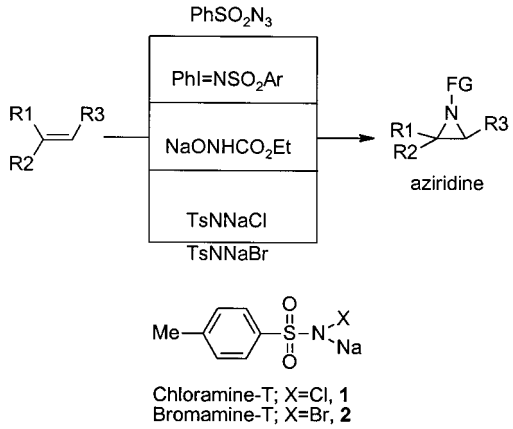

Figure 1.

In our preliminary communication we[11] have demonstrated for the first time the use of Bromamine-T (TsNNaBr) as a superior source of nitrogen in the copper(I)- or copper(II)-catalyzed aziridination of olefins. In this account we present details of this reaction and further applications with this versatile reagent.

Result and Discussion

Although Chloramine-T, **1** (*N*-chloro-*N*-sodio-*p*-toluenesulfonamide), has found several synthetic uses,[10b] its bromo analogue, Bromamine-T, **2**, has been mainly utilized as a titrant in oxidimetric estimations[12] and occasionally as an oxidant.[13] Komatsu and co-workers have recently reported[10a] copper-catalyzed aziridination of olefins with Chloramine-T, **1**, as the source of nitrogen. A range of olefins was subjected to this reaction, and aziridines were isolated in low to moderate yields. Aziridination with some substrates was not so effective with Chloramine-T. For example cyclohexene gave unwanted products probably of allylic amination,[6,7b,c] and 1-decene furnished the corresponding aziridine in only 12% yield. In view of these limitations these reactions were reinvestigated[11] with Bromamine-T, **2**, as the source of nitrogen. During this period, three more accounts were published dealing with aziridination of olefins with Chloramine-T mediated by iodine,[10b] copper catalyst,[14] and one from Sharpless[15a] using phenyltrimethylammonium tribromide (PTAB) as the activator. Recently Sudalai[15b] reported the use of pyridinium hydrobromide perbromide for similar conversion.

Preliminary experiments for comparison of Chloramine-T, **1,** and Bromamine-T, **2**, in the aziridination were carried out with Cu(I)Cl as the catalyst and with styrene as the standard substrate. Under identical conditions, **2** furnished the corresponding aziridine in substantially higher yield compared to that with **1** as the nitrogen source. Improvement in the efficiency of aziridination with **2** was more evident in the case of cyclooctene where the yield was almost doubled as compared to that with **1**. Aziridination of cyclooctene performed with **2** in the presence of $Cu(II)Cl_2$ as the catalyst proceeds with almost the same efficiency. This is probably because Bromamine-T **2** oxidizes cuprous chloride to cupric chloride. The actual catalytic species could be Cu(II) observed by Evans[7b] in the aziridination of olefins with PhINTs.

Table 1. Microwave-Assisted Aziridination of Styrene with Bromamine-T Using Different Catalysts

entry	metal halide[a]	% yield[b]
1	$CuCl_2$	70
2	$NiCl_2$	60
3	$CoCl_2$	56
4	$FeCl_3$	63
5	$MgCl_2$	57
6	$MnCl_2$	54
7	$SrCl_2$	40
8	$CuBr_2$	88
9	$Rh_2(OAc)_4$[c]	30
10	no catalyst	no reaction

[a] A mixture of the catalyst (5 mol %), Bromamine-T (1 equiv), and styrene (5 equiv) in acetonitrile was exposed under microwave for 12 min. [b] Isolated yield. [c] CAUTION! Sparks were observed occasionally.

Microwave-assisted chemical transformations have gained importance in recent years as they expedite the reactions with more efficiency. With an aim to reduce the reaction time and also to achieve aziridination with relatively less reactive olefins, this reaction was investigated under the microwave irradiation. Standard reaction of styrene with **2** catalyzed by CuCl clearly indicates marked improvement of this reaction. To the best of our knowledge, this is the first report of microwave-assisted catalytic aziridination of olefins.

One of the objectives of the current work was also to establish the most suitable metal catalyst for aziridination of olefins with **2** as the source of nitrogen. With this in view, styrene was subjected to aziridination with **2** and catalyzed by different metal salts under microwave irradiation (Table 1).

It is evident from this study that the halides of copper are ideal candidates as catalysts for this reaction. Having established the superiority of copper halides as the catalysts, the mechanistic aspects of this important conversion were also investigated. By analogy with a well-established mechanism of metal-catalyzed cyclopropanation of olefins, one possibility is the transfer of nitrene generated from **1** or **2** in the presence of Cu catalyst, via a Cu-nitrenoid intermediate. Experimental evidence of this possibility was furnished by Jacobsen et al.[17] in their work on the asymmetric aziridination with PhINTs as a nitrene precursor. Reaction of Chloramine-T with an olefin in the presence of a positive halogen results in the formation of aziridine. Komatsu and co-workers[10b] used iodine to initiate the reaction and suggest the formation of a cyclic iodonium intermediate, followed by nucleophilic addition of the nitrogen to give aziridine. Sharpless[15] performed this reaction with PTAB, a phase-transfer agent, which supplies bromonium ion to catalyze the reaction in more or less the same fashion. The Cu-

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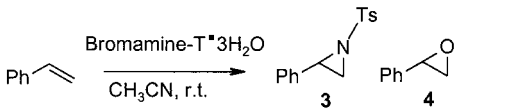
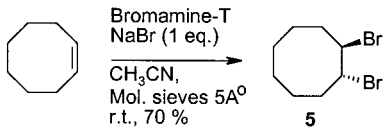
Scheme 2



Scheme 3



catalyzed aziridination of olefins could follow an alternative Lewis acid mechanism. Support for this mechanism is available in the literature[18] in the form of examples of epoxidation and aziridination with PhINTs catalyzed by simple Lewis acids.

Recently, Taylor and co-workers[14] have reported Cu-catalyzed aziridination and amination of alkenes with hydrated Chloramine-T. Aziridination of styrene with commercial Chloramine-T trihydrate did not give epoxide even in the absence of molecular sieves, suggesting a possible Cu-nitrenoid mechanism. Similarly the reaction of styrene with Bromamine-T trihydrate in the presence of $CuCl_2$ as the catalyst in acetonitrile without molecular sieves was carried out. Although aziridine **3** was isolated, no styrene oxide could be detected in the reaction mixture (Scheme 2), lending support to the Cu-nitrenoid mechanism.

Aziridination did not proceed in the absence of catalyst both with **1**[10b] as well as with **2**. Aziridination of cyclooctene with both CuCl and $CuCl_2$ proceeded in good yield, but with 1 equiv of NaBr and without Cu-catalyst *trans*-1,2-dibromocyclooctane was obtained as the sole product (Scheme 3). We believe Bromamine-T serves as the source of bromonium ion in the absence of copper halide.

These observations are in agreement with the mechanism suggested by Jacobsen[17] which involves a copper-nitrenoid intermediate similar to generally accepted analogous copper-carbenoid intermediate for the cyclopropanation mechanism.[3b]

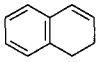
A variety of substrates were examined for aziridination with Chloramine-T, **1**, and with Bromamine-T, **2**, in the presence of copper catalyst. Improvement in the efficiency with **2** compared to **1** in the case of styrene and cyclohexene has already been mentioned. Similar pattern was observed in a number of structurally diverse substrates (Table 2). It was interesting to note that there was no aziridination with less reactive cinnamates with **1** as well as with **2** in the presence of $CuCl_2$ and $CuBr_2$. However, reaction proceeded under microwave irradiation with $CuBr_2$ to yield the aziridine, albeit in poor yield. In general, it was observed that microwave-mediated aziridination of olefins with Bromamine-T was effective in a very short reaction time.

Reactions characteristic of ultrasound irradiation have been named sonochemical transformations and have become topical in recent years.[19] Sonication induces a specific chemical reactivity, although the detailed mechanism of the sonochemical excitation is still unclear. Aziridination of styrene with $CuCl_2$ as catalyst under ultrasound irradiation in the presence of Bromamine-T was found to give good yield in short time (Scheme 4).

Evaluation of aziridination under this improved condition was of particular interest. Thus, Cu-catalyzed aziridination of methyl cinnamate with Bromamine-T as a nitrogen source resulted in selective formation of *trans*-aziridine as depicted in Scheme 5. This is in contrast to the results of same reaction under microwave irradiation, where a mixture of cis and trans isomers of aziridine was obtained. Such results may be attributed to the difference in the activation mechanisms of both the processes (Scheme 5).

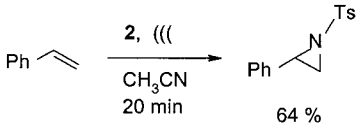
Recently, three independent groups led by Komatsu, Sharpless, and Sudalai have reported aziridination of olefins catalyzed by iodine,[10b] phenyltrimethylammonium tribromide (PTAB),[15a] and pyridinium hydrobromide perbromide,[15b] respectively. All these reactions proceed by an ionic mechanism. Application of a cheap and

Table 2. Comparison of 1 and 2 in the Aziridination of Olefins

Entry	Substrate	% Yield[a] of aziridine with 1[b]	with **2** (microwave[c])
1.		31	48 (70)
2.		75	81 (88)
3.		30[d]	45
4.		67	60 (70)
5.		38	70[e] 72 (81)
6.		< 5[d]	55
7.		45	73
8.	$H_{17}C_8$	12[d]	20 (80)
9.	Ph  CO_2Me	no reaction	no reaction (38[f])
10.	Ph  CO_2tBu	no reaction	no reaction (36[f])

[a] Isolated yield. Aziridines are characterized by spectroscopic methods. [b] Taken from the literature.[10a] [c] All the reactions under microwave were catalyzed by $CuCl_2$ (5 mol %) for 12 min; in some experiments longer irradiation resulted in the formation of dark reaction mixtures. [d] Present work with **1**. [e] With $CuCl_2$ (5 mol %). [f] With $CuBr_2$ (20 mol %) with formation of a mixture of cis and trans isomers, detected by NMR.

Scheme 4



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Scheme 5

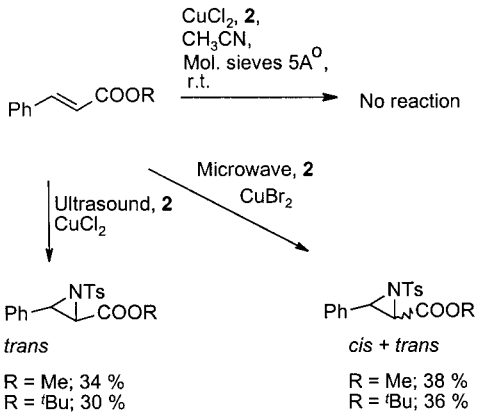
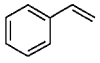
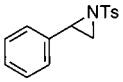
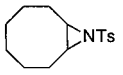
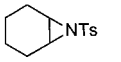
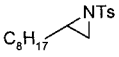
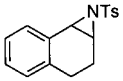


Table 3. Bleaching Powder Initiated Aziridination of Olefins[a]

Entry	Substrate	Product	% Yield
1.			68
2.			73
3.			20
4.			28
5.			80

[a] Reactions were carried out at room temperature in dry acetonitrile with 20% calcium hypochlorite as catalyst. Yields are of isolated product.

commercially available reagent, i.e., calcium hypochlorite [$Ca(OCl)_2$] commonly known as bleaching powder to initiate aziridination of olefins was explored in the present work. Preliminary experiments with both Bromamine-T and Chloramine-T as a nitrogen source gave good yields of aziridines under mild reaction conditions and simple workup procedures. The methodology is convenient and obviates the need for a metal catalyst. Several substrates were screened under similar conditions, and it can be seen from Table 3 that the yields obtained are comparable to those of previous reports using different reagents.

Substitution of benzyl halides or alcohol derivatives by an amine or its equivalent is a general method for the preparation of benzylic amines.[20] Recently, Sharpless[15a] and Taylor[14] have reported both allylic and benzylic amination with Chloramine-T. In our continuing efforts toward application of Bromamine-T in such reactions, benzylic amination was studied, and the preliminary results obtained are presented here.

Tetralin was subjected to benzylic amination with Bromamine-T in the presence of catalytic amount of $Rh_2(OAc)_4$. The expected insertion product was obtained

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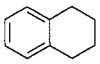
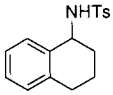
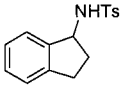
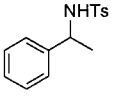
Table 4. Rh-Catalyzed[a] Benzylic Amination with Bromamine-T

Entry	Substrate	Product	% Yield[b]
1.			70(35)[c]
2.			60
3.			33

[a] Reactions were performed in ultrasound (20 min) with 2.5 mol % $Rh_2(OAc)_4$ in acetonitrile. [b] Isolated yield. [c] Yield in parentheses refers to the reaction at room temperature for 12 h.

albeit in poor yield. Subjecting the same reaction under ultrasound conditions resulted in enhanced yields of the desired product (Table 4). Under optimized conditions, amination of ethyl benzene and indane also proceeded smoothly to yield the desired products. These Rh-catalyzed insertion reactions of Bromamine-T are similar to the ones observed by Müller et al.[8b] though with a different source of nitrene.

The successful ultrasound induced benzylic amination with Bromamine-T in the presence of $Rh_2(OAc)_4$ has a wide scope and has opened several possibilities for further exploitation. This can be a practical approach toward preparation of benzylic amines.

In conclusion, the superiority of Bromamine-T over Chloramine-T in the aziridination of olefins has been amply demonstrated. Application of microwave and ultrasound techniques has resulted in enhanced yields of aziridines in shorter reaction times.

Experimental Section

The ^1H NMR spectra were recorded in $CDCl_3$ with TMS as internal standard on a Bruker spectrometer (200 MHz). Sonication experiments were carried out using an ultrasonic bath (Sheishin model) operating at 36 kHz. The bulk temperature during sonication was kept at 25 °C. Microwave irradiations were carried out in a Batliboi Eddy domestic microwave oven operating at 2450 MHz, and reactions were performed at 30% of its full power. Column chromatography was performed with Merck silica gel using a gradient method with a mixture of light petroleum ether and ethyl acetate (5 to15%) as eluent. Acetonitrile was distilled over CaH_2 and stored over molecular sieves.

Typical Procedure for Aziridination at Room Temperature. A two-necked 25 mL round-bottomed flask was charged with Bromamine T (100 mg, 0.0004 mol), 5 Å powdered molecular sieves (10 mg), and anhydrous $CuCl_2$ (5 mg, 0.00004 mol). Anhydrous acetonitrile (5 mL) and styrene (0.23 mL, 0.002 mol) were then added, and the suspension was stirred for 12 h at room temperature under inert atmosphere. It was diluted with dichloromethane and passed through a short plug of silica gel. The crude reaction mixture was purified by silica gel column chromatography to yield 45 mg (45%) of the pure aziridine product.

Representative Procedure of Aziridination Using Bleaching Powder. A two-necked 25 mL round-bottomed flask was charged with of Bromamine-T (100 mg, 0.0004 mol), 5 Å powdered molecular sieves (10 mg), and commercial calcium hypochlorite (5 mg, 10 mol %). Anhydrous acetonitrile (5 mL) was then added, and after 5 min, styrene (0.2 mL,

0.002mol) was added and the suspension was stirred at room temperature for 12 h under inert atmosphere. The crude reaction mixture was passed through a short pad of silica gel and the solvent concentrated in a vacuum. The crude product obtained was purified by chromatography on silica gel to yield 68 mg (68%) of the pure aziridine.

Typical Procedure of Aziridination Using Ultrasound. Styrene (0.2 mL, 0.002mol), Bromamine-T (100 mg, 0.0004 mol), and $CuCl_2$ (5 mg, 10 mol %) in 5 mL of anhydrous acetonitrile were taken in a glass tube which was then irradiated in the sonication bath for 20 min under dry atmosphere. The catalyst was filtered off, and the crude reaction mixture was purified using silica gel column chromatography to yield 69 mg (64%) of the aziridine.

Typical Procedure of Aziridination under Microwave Conditions. A 25 mL pear-shaped round flask was charged with Bromamine-T (50 mg, 0.0002 mol), 5 Å powdered molecular sieves (5 mg), and $CuBr_2$ (5.0 mg, 10 mol %). Dry acetonitrile (2 mL) and styrene (0.1 mL, 0.001mol) were then added, and the reaction mixture was irradiated for 12 min in domestic microwave oven. After cooling, the contents of the flask were passed through a short plug of silica gel. The pure product, 44 mg (88%) was obtained by column chromatography.

Typical Procedure for Benzylic Amination under Sonication. To a mixture of $Rh_2(OAc)_4$ (4.0 mg, 2.5 mol %), molecular sieves (40 mg), and tetralin (0.19 mL, 0.001mol) in dry acetonitrile (2 mL) was added Bromamine-T (100 mg, 0.0004 mol). The reaction mixture was subjected to ultrasound radiation for 20 min. After filtration, the reaction mixture was subjected to purification by column chromatography to give 77 mg of the product (70%)

Spectral Data of Selected Compounds.

***N*-(*p*-Tolylsulfonyl)-2-phenylaziridine** (Tables 1 and 2; entry 1):[7c] IR ν 3017, 1327, 1217, 1161, 916, 783, 769, 713, 696, 665 cm^{-1}. ^1H NMR δ 8.20 (d, J = 10.8 Hz, 2H), 7.59 (m, 7H), 4.18 (dd, J = 9.7, 6.5 Hz, 1H), 3.39 (d, J = 9.8 Hz, 1H), 2.82 (s, 3H), 2.72 (d, J = 6.3 Hz, 1H). MS m/z (%) 273 (M^+, 5), 155 (4), 118 (83), 91 (100).

***N*-(*p*-Tolylsulfonyl)-2-phenyl-2-methylaziridine** (Table 2; entry 2):[7c] IR ν 3060, 3028, 2992, 1440, 930 cm^{-1}. ^1H NMR δ 7.80 (d, J = 8 Hz, 2H), 7.55−7.15 (m, 9H), 2.81 (s, 3H), 2.16 (s, 3H), 2.01 (s, 3H). MS m/z (%) 287 (M^+, 1), 256 (1), 222 (10), 188 (40), 171 (65), 155 (100).

1,1a,6,6a-Tetrahydroindeno[1,2-*b*]aziren-1-yl-4-methylphenyl sulfone (Table 2, entry 3):[22]IR ν 3072, 2735, 2025, 1115, 960 cm^{-1}. ^1H NMR δ 7.70 (m, 4H), 6.92 (m, 4H), 5.42 (m, 3H), 3.50 (m, 1H), 3.10 (m, 1H), 2.70 (s, 3H). Mass, m/z (%) 285 (10), 252 (40), 221 (35), 167 (60), 91 (100).

***N*-(*p*-Tolylsulfonyl)-1,2,3,4-tetrahydronaphthalene-1, 2-amine** (Table 2; entry 4):[7c] IR ν 1599, 1150, 1092, 990, 665 cm^{-1}. ^1H NMR δ 7.85 (d, J = 8.5 Hz, 2H), 7.25−7.15 (m, 6H), 3.80 (d, J = 7.7 Hz, 1H), 3.55 (d, J = 6.9 Hz, 1H), 2.70 (dt, J = 15.5 and 5.2 Hz, 1H), 2.60 (dd, J = 16.5 and 6.2 Hz, 1H), 2.49 (s, 3H), 2.32 (dd, J = 15.2 and 5.3 Hz, 1H), 1.71 (dt, J = 13.7 and 5.4 Hz, 1H). MS m/z (%) 299 (M^+, 1), 226 (1.5), 144 (100), 117 (67), 91 (32).

***N*-(*p*-Tolylsulfonyl)-9-azabicyclo[6.1.0]nonane** (Table 2, entry 5):[7c] IR ν 3028, 2982, 2936, 1600, 1498, 1160, 610 cm^{-1}. ^1H NMR δ 7.77 (d, J = 8.3 Hz, 2H), 7.31−7.24 (m, 7H), 4.44 (d, J = 3.9 Hz, 1H), 3.85 (s, 3H), 3.53 (d, J = 4 Hz, 1H), 2.41 (s, 3H), 1.59−1.20 (m, 12H). MS m/z (%), 278 (2), 259 (M^+, 3), 210 (12), 125 (100), 91 (45), 55 (58).

***N*-(*p*-Tolylsulfonyl)-7-azabicyclo[4.1.0]heptane** (Table 2, entry 6):[7c] IR ν 3020, 1600, 1440, 1395, 965, 920 cm^{-1}. ^1H NMR δ 7.81 (d, J = 9.8 Hz, 2H), 7.40 (d, J = 8.9 Hz, 2H), 3.10 (t, 3H), 2.49 (s, 3H), 1.81 (m, 4H), 1.5−1.4(m, 4H). MS, m/z (%) 252 (M + 1, 1), 210 (2), 155 (6), 96 (100), 91 (40), 69 (40), 65 (17).

3-(4 Methylphenylsulfonyl)-3-azatricyclo[3.2.1.0]octane (Table 2; entry 7):[7c] IR ν 3016, 1300, 1280, 1080,960 cm^{-1}. ^1H NMR δ 7.97 (d, J = 8 Hz, 2H), 6.77 (d, 2H), 2.87 (s, 2H), 1.98 (s, 3H), 1.86 (s, 4H), 1.45 (dt, J = 2.0 Hz, 1H), 0.97 (m, 2H), 0.8 (m, 2H). MS m/z (%) 263 (M + 1, 1), 199 (18), 155 (30), 91 (100), 60 (35).

***N*-(*p*-Tolylsulfonyl)-2-octylaziridine** (Table 2; entry 8):[21] IR ν 3017, 1327, 1217, 1161, 916, 783, 769, 713, 696, 665 cm^{-1}. ^1H NMR δ 8.20 (d, J = 10.8 Hz, 2H), 7.59 (m, 7H), 4.18 (dd, J = 9.7 and 6.5 Hz, 1H), 3.39 (d, J = 9.8 Hz, 1H), 2.82 (s, 3H), 2.72 (d, J = 6.3 Hz, 1H). MS m/z (%) 273 (M^+, 5), 155 (4), 118 (83), 91 (100), 65 (21).

***N*-(*p*-Tolylsulfonyl)-2-carbomethoxy-3-phenylaziridine** (Table 2; entry 9):[7c] IR ν 3068, 3021, 2960, 1750, 1600, 1412, 1167, 906 cm^{-1}. ^1H NMR (trans isomer) δ 7.77 (d, J = 8.3 Hz, 2H), 7.31−7.24 (m, 7H), 4.44 (d, J = 3.9 Hz, 1H), 3.85 (s, 3H), 3.53 (d, J = 4.0 Hz, 1H), 2.41 (s, 3H). ^1H NMR (cis isomer) δ 7.90 (d, J = 8 Hz, 1H), 7.40 (d, J = 8 Hz, 1H), 7.25 (m, 7H), 4.10 (d, J = 8.2 Hz, 1H), 3.70 (d, J = 7.8 Hz, 1H), 3.50 (s, 3H), 2.49 (s, 3H). MS m/z (%) 332 (M + 1, 5), 331 (M^+, 8), 300 (10), 176 (75), 144 (25), 116 (100), 91 (70), 65 (30).

***N*-(*p*-Tolylsulfonyl)-2-carbo-(2-methyl-2-propoxy)-3-phenylaziridine** (Table 2; entry 10):[7c] IR ν 3028, 1740, 1085, 910 cm^{-1}. ^1H NMR δ 7.80 (d, J = 8 Hz, 2H), 7.40−7.00 (m, 7H), 4.44 (d, J = 2 Hz, 1H), 3.40 (d, J = 2 Hz, 1H), 2.49 (s, 9 H), 1.5 (s, 9H). MS m/z (%), 373 ($M^{+\cdot}$ 0. 5), 300 (18), 273 (18), 162 (70), 91(100).

1-{*N*- (*p*-Tolylsulfonyl)amino}-1,2,3,4- tetrahydronaphthalen-1-yl (Table 4; entry 1):[14] IR ν 3361, 3236, 3000, 2847, 1140, 742 cm^{-1}. ^1H NMR δ 7.90 (d, J = 8 Hz, 2H), 7.40 (d, J = 8 Hz, 2H), 7.30−6.85 (m, 4H), 4.85 (d, J = 6 Hz, 2H), 4.50 (m, 1H), 2.90−2.64 (m, 2H), 2.45 (s, 3H), 1.90−1.68 (m, 4H). Mass m/z (%), 301 (M^+, 2), 235 (20), 155 (40), 146 (90), 130 (100), 91 (80).

1-{*N*-(*p*-Tolylsulfonyl)amino}indane (Table 4; entry 2):[14] IR ν 3246, 3047, 2968, 1730, 1400, 1125 cm^{-1}. ^1H NMR δ 7.80 (d, J = 8.0 Hz, 2H), 7.40−7.10 (m, 6H), 5.00 (m, 1H), 4.62 (m, 1H), 3.20 (m, 1H), 3.15 (m, 1H), 2.42 (s, 3H), 2.30−1.60 (m, 2H). MS m/z (%), 287 (M^+, 0.3), 149 (15), 133 (100), 115 (50), 91 (12), 77 (35).

1-{*N*-(*p*-Tolylsulfonyl)amino}-1-phenylethyl (Table 4; entry 3):[14] IR ν 3368, 3319, 2970, 1360, 752 cm^{-1}. ^1H NMR δ 8.00 (s, 1H), 7.65 (d, J = 4 Hz, 2H), 7.50−7.00 (m, 5H), 4.75 (d, J = 6 Hz, 1H), 4.50 (m, 1H), 2.46 (s, 3H), 1.48 (d, J = 8 Hz, 3H). MS m/z (%), 275 (M^+, 0.5), 260 (95), 210 (1), 165 (1), 155 (48), 120 (50), 104 (30), 91 (100), 77 (22).

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