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TIN(II) IODIDE-CATALYZED SELECTIVE AZIRIDINATION OR 1,2-DIAMINATION OF ALKENES WITH CHLORAMINE-T

Yoshiro Masuyama,* Masaru Ohtsuka, Masaru Harima, and Yasuhiko Kurusu

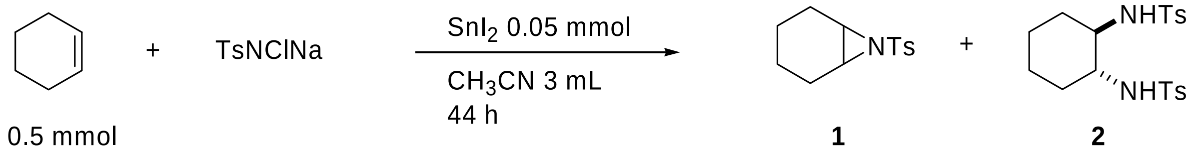
Department of Chemistry, Sophia University, 7-1 Kioicho, Chiyoda-ku, Tokyo 102-8554, Japan; y-masuya@sophia.ac.jp

Abstract – Tin(II) iodide selectively catalyzes reactions of alkenes in acetonitrile to afford the corresponding aziridines by the use of one equimolar amount of Chloramine-T [$Ts(Cl)N^-$] at room temperature and to afford the corresponding 1,2-diamines by the use of excess Chloramine-T at 50 °C.

Aziridines have been applied to the synthesis of a variety of nitrogen-containing compounds as building blocks, and effective methodologies for aziridine synthesis continue to be required.[1] Among reported methodologies, aziridinations of alkenes with Chloramine-T [Ts(Cl)NNa] have the advantages of the inexpensiveness and tractability of Chloramine-T and the simplicity of operation.[2,3] In the course of studying carbonyl allylations with tin(II) iodide, we presumed that triiodostannate(II) (I_3Sn^-) was prepared from tin(II) iodide and iodide sources and then caused nucleophilic substitution to allyl halides to produce an actual allylating agent, allyltriiodotin(IV).[4] Thus we hoped that $Ts(Cl)N^-$ instead of I^- could react with SnI_2 to prepare (*N*-chloro-*N*-tosylamino)diiodostannate(II) [$Ts(Cl)N\text{-}Sn^-I_2$]. If the $Ts(Cl)N\text{-}Sn^-I_2$ could be converted into $I_2Sn{=}NTs$ that could function as a nitrene source, SnI_2 would serve as a catalyst for the aziridination of alkenes with Chloramine-T, similarly to a copper(I) complex.[2c]

The reactions of cyclohexene (0.5 mmol) with commercially available Chloramine-T trihydrate ($TsNClNa{\cdot}3H_2O$) were investigated in the presence of a catalytic amount of SnI_2 (0.05 mmol) in acetonitrile. The results are summarized in Table 1. A typical procedure is as follows (Entry 1): To the solution of tin(II) iodide (19 mg, 0.05 mmol) and Chloramine-T trihydrate (0.14 g, 0.5 mmol) in acetonitrile (3 mL) at room temperature was added cyclohexene (41 mg, 0.5 mmol). The solution was stirred at room temperature for 44 h. Usual work-up and purification by column chromatography on silica gel (hexane : ethyl acetate = 1 : 2) and HPLC (Japan Analysis Industry Co. Ltd., LC-908) afforded the corresponding aziridine (**1**) (63 mg, 50%) and the corresponding *anti*-1,2-diamine (**2**) (10 mg, 5%). In this

Table 1. SnI_2-Catalyzed aziridination and 1,2-diamination of cyclohexene with Chloramine-T



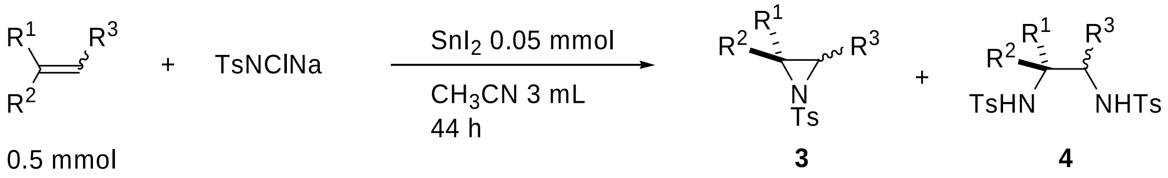
Entry	Chloramine-T / mmol	Temp / °C	Yield/ %^{a}	
			1	2^b
1	0.5	r. t.	50(60)^c	2(5)^c
2	1.0	r. t.	53	10
3	1.0	50	61	25
4	2.0	50	0(0)^d	71(66)^d
5	2.0	80	0	40

[a] Isolated yields. [b]See ref. 5. [c]The figures in parentheses are yields in the reaction with cyclohexene (3.0 mmol), Chloramine-T (3.0 mmol) and SnI_2 (0.1 mmol). [d]The figures in parentheses are yields in the reaction with cyclohexene (3.0 mmol), Chloramine-T (6.0 mmol) and SnI_2 (0.1 mmol) in CH_3CN (5 mL).

manner, namely by the use of one equimolar amount of Chloramine-T (0.5 mmol) at room temperature, aziridine (**1**) was selectively produced. Increasing the quantity of Chloramine-T and elevating the reaction temperature enhanced the yield of *anti*-1,2-diamine (**2**) (Entries 2-5). The *anti*-1,2-diamine (**2**) was selectively produced with 2.0 mmol of Chloramine-T at 50 °C (Entry 4).[5] No reactions in other solvents such as THF, 1,4-dioxane, and 1,3-dimethyl-2-imidazolidinone occurred even with excess Chloramine-T and even at 50 °C.

Aziridinations or 1,2-diaminations of some alkenes were investigated under the same conditions as those of Entry 1 in Table 1 or under the same conditions as those of Entry 4 in Table 1 respectively. The results are summarized in Table 2. Monosubstituted alkenes (Entries 1, 3-6, 8, and 10-12 in Table 2), 1,1-disubstituted alkene (Entries 2 and 9 in Table 2), and 1,2-disubstituted alkenes (Entries 1 and 4 in Table 1 and Entries 7 and 13 in Table 2) can be applied to the selective SnI_2-catalyzed aziridination or 1,2-diamination with Chloramine-T. The aziridination selectively occurred with one equimolar amount of Chloramine-T to alkenes at room temperature, while the use of excess Chloramine-T at 50 °C led to selective 1,2-diamination.[5] Since the reactivity of an aliphatic monosubstituted alkene such as 1-octene was low (Entry 5), 1.0 mmol of Chloramine-T was employed to enhance the yield (Entry 6). In the aziridination of 1-octene (0.5 mmol) with Chloramine-T (1.0 mmol) at room temperature for 44 h in acetonitrile (3 mL), tin(II) iodide as a catalyst is superior to other tin(II) halides; $SnBr_2$ (24%), $SnCl_2$ (22%), and SnF_2 (0%). 1-[(4-Methylphenyl)sulfonyl]-2-phenylaziridine (**3**: R^1=Ph; R^2, R^3=H) underwent ring-opening with Chloramine-T in the absence of tin(II) iodide to produce the corresponding 1,2-diamine (**4**: R^1=Ph; R^2, R^3=H) in 62% yield (Scheme 1). The use of *p*-toluenesulfonamide instead of

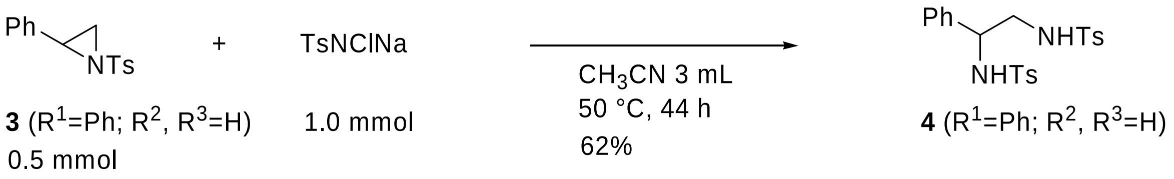
Table 2. Selective aziridinations and 1,2-diaminations of alkenes with Chloramine-T



Entry	R^1	R^2	R^3	Chloramine-T /mmol	Temp /°C	Yield/ %[a]	
						3	**4**
1	C_6H_5	H	H	0.5	r. t.	75	3
2	C_6H_5	CH_3	H	0.5	r. t.	54(44)[b]	0(0)[b]
3	$4\text{-}CH_3H_6H_4$	H	H	0.5	r. t.	71	4
4	$4\text{-}ClC_6H_4$	H	H	0.5	r. t.	72(68)[b]	4(4)[b]
5	C_6H_{13}	H	H	0.5	r. t.	26	8
6	C_6H_{13}	H	H	1.0	r. t.	48	4
7[c]	C_5H_{11}	H	CH_3	0.5	r. t.	66[d]	0
8	C_6H_5	H	H	2.0	50	0	69
9	C_6H_5	CH_3	H	2.0	50	0	49
10	$4\text{-}CH_3H_6H_4$	H	H	2.0	50	0	68
11	$4\text{-}ClC_6H_4$	H	H	2.0	50	3	66
12	C_6H_{13}	H	H	2.0	50	0	49
13[c]	C_5H_{11}	H	CH_3	2.0	50	13	60[e]

[a] Isolated yields. [b] The figures in parentheses are yields in the reactions with alkene (3.0 mmol), Chloramine-T (3.0 mmol), and SnI_2 (0.1 mmol). [c] (*E*)-2-octene : (*Z*)-2-octene = 19 : 81. [d] syn : anti = 4 : 1.[3b] [e] The diastereomer ratio is 4 : 1. [d,e] The diastereomer ratios were determined by ^1H NMR analysis (JEOL JNM-LA500).

Chloramine-T caused no ring-opening reaction of **3** (R^1=Ph; R^2, R^3=H) in the presence of SnI_2 under the similar conditions. These results suggest that aziridines, prepared from alkenes and Chloramine-T with SnI_2, undergo nucleophilic attack of another Chloramine-T to afford the corresponding 1,2-diamines.[6]



Scheme 1. Ring-opening of 1-[(4-methylphenyl)sulfonyl]-2-phenylaziridine with Chloramine-T

In summary, tin(II) iodide catalyzes aziridination of alkenes with one equimolar amount of commercially available Chloramine-T trihydrate ($TsNClNa \cdot 3H_2O$) to the alkenes, and the use of excess Chloramine-T leads to 1,2-diamination of alkenes *via* the aziridination.

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