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Silica gel induced cleavage of aziridines by aromatic amines under solvent free conditions

R. Vijaya Anand, Ghanshyam Pandey and Vinod K. Singh*

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

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Abstract—A variety of aziridines were opened in an efficient manner with aromatic amines using silica gel under solvent free conditions. © 2002 Elsevier Science Ltd. All rights reserved.

Ring opening of aziridines with nucleophiles is an important transformation in organic synthesis and it is usually carried out by means of Lewis acids.[1,2] If the nucleophiles are amines, the products become diamines which are a synthetically important class of compounds. Recently, the ring opening of aziridines by amines has been reported in the presence of ytterbium triflate,[2a,2b] copper(II) and tin(II) triflates[2c] in an appropriate solvent. However, there is no report in the literature where this type of aziridine cleavage has been achieved using silica gel under solvent free conditions. In this paper we report, for the first time, the opening of aziridines with aromatic amines with silica gel under solvent free conditions.

A variety of aziridines were synthesized from the corresponding amino alcohols[3] in one step using MsCl (1.1 equiv.) and Et_3N (2.5 equiv.) in pyridine (as solvent) at room temperature and then subjected to the cleavage reaction with amines by means of silica gel. In most cases, a high yield of the ring-opened product was obtained (Table 1). In the cases of acyclic terminal aziridines (entries 19 and 20), the reaction was highly regioselective as only one product was isolated. It was observed that if a solvent such as ether was used, the cleavage of the aziridine became sluggish, and even after 2 days the reaction was not complete (50–60% conversion). An important feature of the reaction was that the highly deactivated amine such as *p*-nitroaniline also reacted, although the isolated yield was not high (32%, entry 3). An unusual feature of this reaction is that only aromatic amines opened the aziridines. Aliphatic amines such as diethylamine, *n*-butylamine, benzylamine and pyrrolidine failed to react with aziridines at room temperature. When entry 1 was repeated with a mixture of aniline and benzylamine (1:1 ratio; 1.2 mmol of each amine), only the diamine **1a** was obtained in 81% yield. Aniline reacted with the aziridine, but benzylamine remained unreacted. This observation indicated that the methodology will be very useful for the preferential cleavage of aziridines by aromatic amines. The present methodology for solvent-free cleavage of aziridines by aromatic amines over aliphatic amines should find application in organic synthesis, and to the best of our knowledge, is unprecedented in the literature.

General procedure: A mixture of an aziridine (1 mmol), an aromatic amine (1.2 mmol) and silica gel (500 mg; activated at 120°C under vacuum for 6 h) was taken in a 5 mL R.B. flask and the solid shaken till the reaction was complete (disappearance of aziridine spot on TLC plate). The silica gel–reaction mixture was loaded onto a small silica gel column and eluted with ethyl acetate–petroleum ether to afford the pure diamines.[4]

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* Corresponding author. Fax: 91-512-597436; e-mail: vinodks@iitk.ac.in

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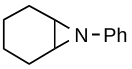
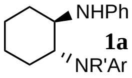
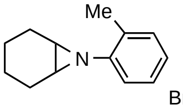
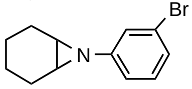
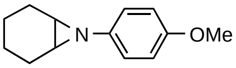
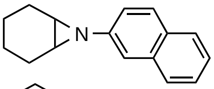
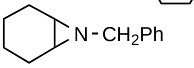
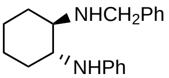
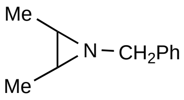
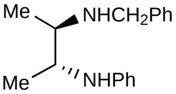
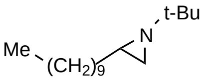
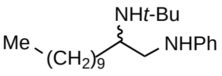
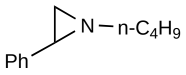
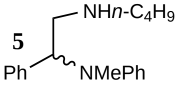
Table 1. Silica gel catalyzed aziridine opening with aromatic amines under solvent free conditions at rt

Entry	Aziridines	Diamines	Time	Isolated Yield (%)
1.		 **1a** R'=H Ar=Ph	1 h	91
2.	"	**1b** R'=Me; Ar=Ph	1 h	87
3.	"	**1c** R'=H; Ar=C_6H_4-*p*-NO_2	8 h	32
4.	"	**1d** R'=H; Ar=C_6H_4-*o*-Me	1.5 h	86
5.	"	**1e** R'=H; Ar=C_6H_4-*m*-Cl	1.5 h	78
6.	"	**1f** R'=H; Ar=C_6H_3-*m*-Br	1.5 h	95
7.	"	**1g** R'=H; Ar=C_6H_4-*p*-OMe	1.5 h	90
8.	"	**1h** R'=H; Ar=β-naphthyl	2 h	85
9.	"	**1i** R'=H; Ar=*o*,*o*'-dimethyl Ph	1.5 h	84
10.	"	**1j** R'=Et; Ar=Ph	1 h	90
11.	"	**1k** R'=H; Ar=*o*,*o*'-diisopropyl Ph	2 h	77
12.	"	**1l** R'=H; Ar=2-pyridine-5-Cl	8 h	58
13.		**1d**	1 h	75
14.		**1f**	2 h	70
15.		**1g**	1 h	89
16.		**1h**	5 h	66
17.		**2** 	2 h	91
18.		**3** 	24 h	45
19.		**4** 	10 h	35
20.		**5** 	48 h	89

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4. All the compounds gave satisfactory spectroscopic data.