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Toshihiro Isobe, Takeshi Oriyama

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Ring-opening reaction of aziridines with amines under the influence of dimethyl sulfoxide

Toshihiro Isobe, Takeshi Oriyama*

Department of Chemistry, Faculty of Science, Ibaraki University, 2-1-1 Bunkyo, Mito, Ibaraki 310-8512, Japan

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ABSTRACT

The ring-opening reaction of various aziridines with amines proceeded at room temperature to afford the corresponding 1,2-diamines in good to excellent yields using only 3–5 equiv dimethyl sulfoxide (DMSO) to aziridines in hexane. This reaction can be performed with easy handling and proceeds under mild reaction conditions. Also a variety of amines are available as a nucleophile.

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To dedicated to late Tomoko Kakinuma, past member in our laboratory.

Aziridines are versatile intermediates in synthetic organic chemistry.¹ Many nucleophilic ring-opening reactions of aziridines were reported.² Using amines as a nucleophile in the ring-opening reactions of aziridines, 1,2-diamines can be obtained. Synthesizing 1,2-diamines efficiently is important because their building blocks are contained in many biologically and medicinally active compounds such as penicillins, oseltamivir, and other pharmaceuticals.³ Conventional methods of inducing the ring-opening reactions of aziridines with amines require a metal reagent such as Yb(OTf)₃,^{4a} Sn(OTf)₂ or Cu(OTf)₂,^{4b} LiClO₄,^{4c, h} InBr₃,^{4d} LiNTf₂,^{4e} BiCl₃,^{4f} TaCl₅,^{4g} SmI₂,⁴ⁱ or sulfated zirconia.^{4j} Green chemical methods were also reported, but the examination of amines did not widely conducted in most of those methods.⁵

In recent years, dimethyl sulfoxide (DMSO) received renewed attention as a promoter,^{6a, c, e} an oxidant,^{6f, h} and a reactant^{6b, d, g} of efficient organic reactions. We also developed many novel reactions using DMSO and molecular sieves (MS) 4A during the course of our intensive work.⁷ For example, under the influence of DMSO and MS 4A, the Knoevenagel reaction of *N*-tosylimines with active methylene compounds,^{7g} the double Michael addition of dithiols to acetylenic carbonyl compounds,^{7h} and the aza-Henry reaction of *N*-tosylimines with nitroalkanes^{7j} proceeded smoothly to produce the corresponding products without a metal catalyst or base. Based on these investigations,

we undertook the ring-opening reaction of aziridines with amines using DMSO and MS 4A.

Wu *et al.* already reported the ring-opening reaction of aziridines with various nucleophiles in DMSO in 2006,⁵ⁱ but there were still some issues to be resolved: (1) a large amount of DMSO (2.0 mL to 0.25 mmol aziridines) is used; (2) heating (reactions are conducted at 60 °C) is needed; and (3) only aromatic amines can be applied to this reaction. Here, we describe that the ring-opening reaction of various aziridines with aromatic and aliphatic amines proceeding by using only 3–5 equiv DMSO to aziridines at room temperature to afford the corresponding 1,2-diamines in good to excellent yields.

Initially, we attempt the ring-opening reaction of aziridine **1a** (0.30 mmol), which is derived from cyclohexene⁸ with 1.2 equiv benzylamine **2a** in DMSO (1 mL), in the presence of MS 4A (100 mg). As expected, the corresponding 1,2-diamine is obtained in 92% yield (Table 1, entry 1). We subsequently examine the effect of solvents (entries 2–8). Other aprotic polar solvents such as DMF and MeCN give the desired product in lower yields in comparison with DMSO (entries 2 and 3). Using MeOH as a solvent, we obtain the desired product in 45% yield (entry 4). CH₂Cl₂, THF, and toluene are found to be ineffective for this reaction (entries 5–7). To our surprise, in the case of a hexane solvent, the corresponding product is obtained in 75% yield (entry 8). The examination of the solvent reveals that DMSO is suitable for this reaction and hexane also gives comparatively good results.

* Corresponding author. Tel.: +81-29-228-8368; fax: +81-29-228-8403; e-mail: takeshi.oriyama.sci@vc.ibaraki.ac.jp

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