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Iridium-Catalyzed Isomerization of *N*-Sulfonyl Aziridines to Allyl Amines

Albert Cabré,[†] Giuseppe Sciortino,[§,#] Gregori Ujaque,[§] Xavier Verdaguer,[*,†,‡] Agustí Lledós,[*,§] and Antoni Riera[*,†,‡]

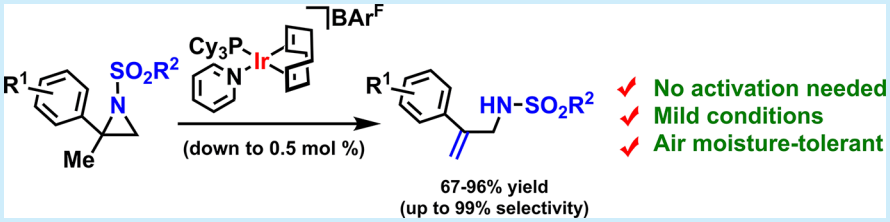
[†]Institute for Research in Biomedicine (IRB Barcelona), The Barcelona Institute of Science and Technology, Baldiri Reixac 10, Barcelona 08028, Spain

[§]Departament de Química, Edifici C.n., Universitat Autònoma de Barcelona, Cerdanyola del Vallès, Barcelona 08193, Spain

[#]Dipartimento di Chimica e Farmacia, Università di Sassari, via Vienna, 2, I-07017 Sassari, Italy

[‡]Departament de Química Inorgànica i Orgànica, Secció Orgànica, Universitat de Barcelona, Martí i Franquès 1, Barcelona 08028, Spain

Supporting Information



ABSTRACT: The Crabtree's reagent catalyzes the isomerization of *N*-sulfonyl 2,2-disubstituted aziridines to allyl amines. The selectivity of allyl amine vs imine is very high (up to 99/1). The unprecedented isomerization takes place in mild conditions without activation of the catalyst by hydrogen. The mechanism has been studied computationally by DFT calculations; instead of the usual hydrogenation of COD, the catalytic species is formed by a loss of the pyridine ligand. Approaching of aziridine to this unsaturated species leads to a carbocation intermediate through a low energy barrier. A metal-mediated tautomerization involving sequentially γ-H elimination and N−H reductive elimination affords selectively the allyl amine. The readiness of the CγH bond to participate in the H elimination step accounts for the selectivity toward the allyl amine product.

Isomerization processes such as thermal rearrangements and catalytic isomerizations are of great synthetic interest due to their perfect atom economy, which makes them ideal transformations from the point of view of sustainability.[1] Terminal olefins,[2] allylic amines,[3] and allylic alcohols[4] are the most common substrates for catalytic isomerization reactions using metal complexes.[5] Epoxides are also excellent substrates for isomerization. The rearrangement of epoxides to carbonyls, referred to as the Meinwald rearrangement,[6] can be promoted by Lewis acids such as $BF_3{\cdot}Et_2O$, lithium salts, or iridium chloride.[7] More recently, Mazet and co-workers uncovered the use of Pd and Ir hydride complexes as efficient catalysts for the isomerization of epoxides.[8,9] The aza-version of the Meinwald rearrangement, however, has received little attention.[10] In 2002, Nakayama et al. described the BF_3-promoted aza-pinacol rearrangement of various *N*-tosyl aziridines to give the corresponding *N*-tosyl imines.[11] Later on, in 2003, Ney and co-workers reported a palladium-catalyzed isomerization of monosubstituted *N*-tosyl aziridines to sulfonyl ketimines.[12]

The ring strain, the facility of preparation, and the utility of the potential products make aziridines the ideal substrates to study new catalytic isomerization reactions. Here, we describe the isomerization of 2,2-disubstituted *N*-sulfonyl aziridines to allylic amines catalyzed by iridium catalysts. The process provides an efficient synthetic strategy for the preparation of many valuable compounds since allyl amines are versatile intermediates[13] in addition to being fragments of several biologically active compounds.[14,15]

We selected 2-methyl-2-phenyl-1-tosylaziridine **1a**, as model substrate since it can be easily prepared from acetophenone by simple Wittig olefination and subsequent aziridination. Aziridine **1a** can, in principle, isomerize to allyl amine **2a**, to imine **3a**, in a similar way to the Meinwald rearrangement of epoxides, or to enamine **4a** (Table 1).

We started with the common catalysts used in the Meinwald rearrangement, namely, $BF_3{\cdot}Et_2O$ and $IrCl_3$. In both cases, a 1:1 mixture of allyl amine (**2a**) and imine (**3a**) was obtained in moderate yield (Table 1, entries 1 and 2). Of note, enamine **4a** was not detected. In our efforts to promote the reaction selectively, our next attempt involved the use of Crabtree's catalyst **5a** (PF_6 salt).[16] This commercial Ir−P,N complex is a well-known hydrogenation catalyst.[17] The CH_2Cl_2 solution of the catalyst was activated by hydrogenation for few minutes and degassed as described for allylic alcohols.[4f,g] Allylic amine was

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