

**Reactivity of 1-arenesulfonyl- and 1-alkyl-2-(bromomethyl)aziridines towards
lithium cuprate reagents**

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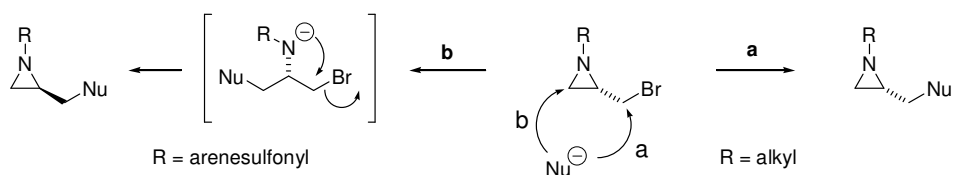
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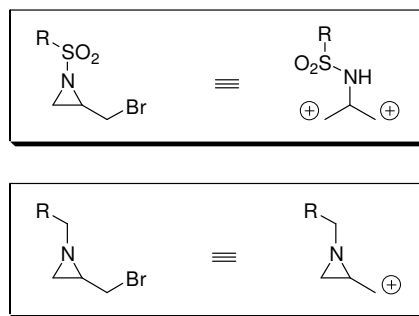
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2-(Bromomethyl)aziridines, a scarcely evaluated class of β -halo amines, are versatile building blocks in organic synthesis due to the presence of three electrophilic centres, allowing the transformation of these building blocks into a variety of target compounds by ring opening reactions at the aziridine moiety and/or substitution reactions at the halogenated carbon atom.

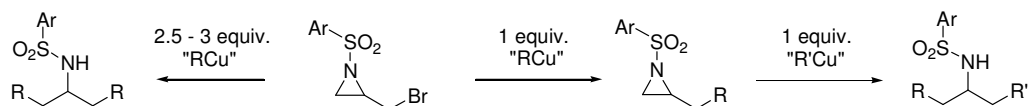
There is, however, a major difference in reactivity between 2-(bromomethyl)aziridines with an electron-withdrawing group at nitrogen (e.g. 1-(arenesulfonyl)aziridines) and those without an electron-withdrawing group at nitrogen (e.g. 1-alkylaziridines). Upon treatment with one equivalent of a nucleophile, 1-(arenesulfonyl)-2-(bromomethyl)aziridines undergo ring opening followed by nucleophilic displacement of the bromide (pathway b), whereas 1-alkyl-2-(bromomethyl)aziridines undergo a direct substitution at the halogenated carbon atom (pathway a).¹



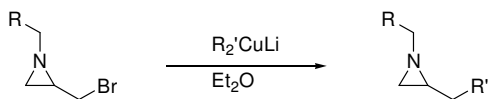
Coupling reactions of 1-(arenesulfonyl)-2-(bromomethyl)aziridines and 1-alkyl-2-(bromomethyl)aziridines with carbon-centered nucleophiles, i.e. lithium cuprate reagents, resulted in a different chemical behavior, pointing to the conclusion that 1-(arenesulfonyl)-2-(bromomethyl)aziridines can be used as synthetic equivalents for the 2-aminopropane dication synthon, whereas 1-alkyl-2-(bromomethyl)aziridines are suitable equivalents for the aziridinylmethyl cation.



1-Arenesulfonyl-2-(bromomethyl)aziridines were successfully transformed into 2-alkylaziridines and symmetrical α -branched N-tosylamides in good yields, with either one or at least two equivalents of reagent, respectively. Also an unsymmetrical amine was prepared by consecutive treatment of 1-tosyl-2-(bromomethyl)aziridine with one equivalent of two different lithium cuprate reagents.²



1-Alkyl-2-(bromomethyl)aziridines proved to be suitable synthetic equivalents for the aziridinylmethyl cation, providing an easy access to 1,2-dialkylaziridines such as 2-ethyl-, 2-pentyl- and 2-(phenylmethyl)aziridines upon treatment with the appropriate lithium dialkylcuprate reagent.³



Keywords: 2-(bromomethyl)aziridines, organocuprate reagents, ring opening, substitution

References

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