Efficient Regio- and Stereoselective Conversions of Oxiranes and Aziridines into β-(Nitrooxy)-Substituted Alcohols and Amines by Using Bismuth Nitrate[1])

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Oxiranes and aziridines efficiently undergo ring opening with bismuth nitrate at room temperature to furnish the corresponding β-(nitrooxy)-substituted alcohols and amines respectively. The conversions are highly regio- and stereoselective and afford the nitrooxy-compounds in excellent yields within a short period of time.

Introduction. – Oxiranes [1] and aziridines [2] are important precursors in organic synthesis. They can easily be cleaved with nucleophiles forming regio- and stereoselective ring-opened products. The ring-opening reactions of these compounds have been studied with various nucleophiles [3]. However, the applications of nitrate ions as nucleophiles for these reactions are limited. β-(Nitrooxy)-substituted alcohols and amines are functionalized alkyl nitrates which can be employed as intermediates in organic synthesis [4]. Oxiranes were previously converted into β-(nitrooxy) alcohols by ring opening with concentrated HNO_3 [5a], ceric ammonium nitrate (CAN) [5b], or NO in air [5c]. All of these methods are associated with several drawbacks. The first method afforded the products in low yields under strongly acidic conditions. CAN converted 'styrene oxide' into benzaldehyde as major product. The reactions of oxiranes with this reagent were generally conducted at high temperature (80°), and regioselectivity for opening of some oxiranes are weak. The conversion of oxiranes [5c] and aziridines [4] with NO required long reaction times (12–32 h). Recently, we have also reported [6] the ring opening of these compounds using zirconyl nitrate to prepare β-(nitrooxy)-substituted alcohols and amines. However, this method was unsuitable for the conversion of 2-aryl-1-tosylaziridines as significant amounts of the corresponding β-amino alcohols were also formed. Moreover, the conversion times with 2-alkylaziridines and bicyclic aziridines were high (4.5–8 h). Thus, we searched for an alternative better method for ring opening of both oxiranes and aziridines with nitrate ions. As a result of our continuous efforts for the synthesis of β-(nitrooxy)-substituted alcohols and amines we discovered that these compounds can efficiently be prepared from oxiranes and aziridines by using bismuth nitrate at room temperature.

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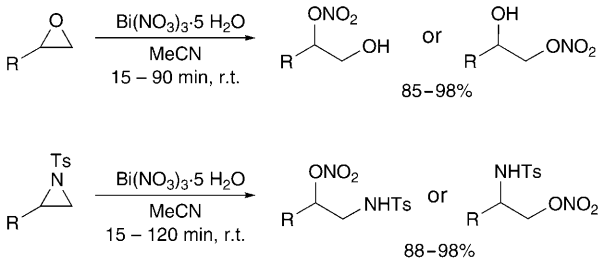
Results and Discussion. – Various oxiranes and *N*-tosylaziridines were treated with bismuth nitrate in MeCN to form the nitrooxy compounds in excellent yields (*Scheme* and *Table*). They were also treated with other, different metal nitrates such as lanthanum nitrate and silver nitrate under similar reaction conditions, but no nitrooxy products could be detected. Bismuth nitrate acted here both as a reagent and as a catalyst. The time required to cleave 2-aryloxiranes and 2-aryl-1-tosylaziridines was only 15–20 min. Bicyclic oxiranes also underwent cleavage within similar times. However, in the case of 2-alkyloxiranes as well as 2-alkyl-1-tosylaziridines, somewhat longer times (1.5–2 h) were required. Contrary to our previous observation [6], no β-amino alcohols were obtained by ring opening of 2-arylaziridines with bismuth nitrate. Thus, the present method represents an improved protocol for the synthesis of β-(nitrooxy) alcohols and amines.

Scheme 1



The conversions of both oxiranes and aziridines took place with high regio- and stereoselectivity. The 2-aryloxiranes and 2-aryl-1-tosylaziridines yielded the products formed by opening at the benzylic ring position, while 2-alkyloxiranes and 2-alkyl-1-tosylaziridines furnished the products formed by cleavage at the unsubstituted ring position. Bicyclic oxiranes and aziridines underwent stereoselective ring cleavage in *anti* manner forming the products with *trans*-configuration. The structures and configurations of the products were confirmed by comparison of their spectral (IR, ^{1}H- and ^{13}C-NMR, and MS) values with those reported earlier [6].

In conclusion, we reported an improved and advantageous method for the ring opening of oxiranes and aziridines by using bismuth nitrate at room temperature to form the corresponding β-(nitrooxy)-substituted alcohols and amines, respectively, in high yields and with impressive regio- and stereoselectivity. The method is equally applicable for the conversion of 2-aryl- and 2-alkyloxiranes and -aziranes and of bicyclic oxiranes and aziridines.

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Experimental Part

General Procedure. To a soln. of an oxirane or 1-tosylaziridine (1 mmol) in MeCN (5 ml), bismuth nitrate (1.2 mmol) was added. The mixture was stirred at r.t., and the reaction was followed by TLC.

Table. *Bismuth Nitrate Mediated Ring Opening of Oxiranes and Aziridines*[a])

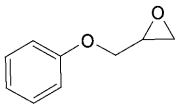
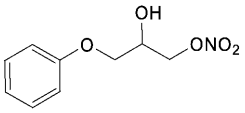
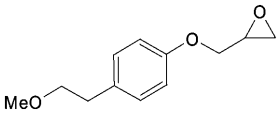
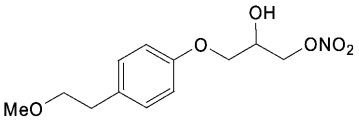
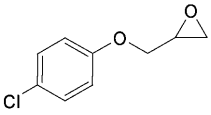
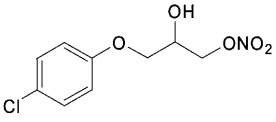
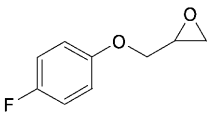
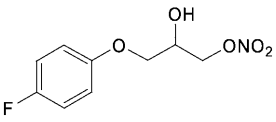
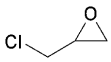
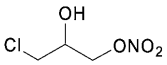
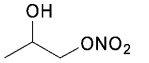
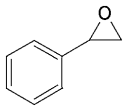
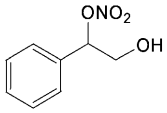
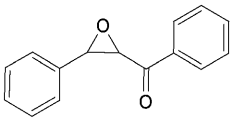
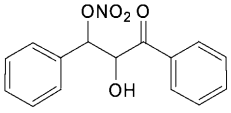
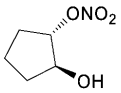
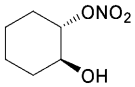
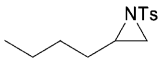
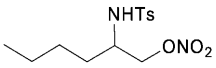
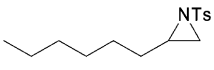
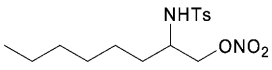
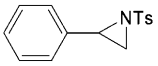
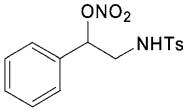
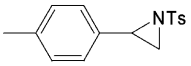
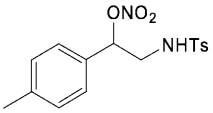
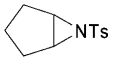
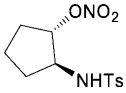
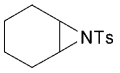
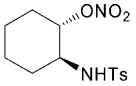
Oxirane or aziridine	Product	Time [min]	Isolated yield [%][b])
		80	90
		90	89
		90	91
		90	88
		45	94
		40	92
		15	98
		20	85
		20	96
		20	98
		120	90[c])
		120	83[c])
		15	98

Table (cont.)

Oxirane or aziridine	Product	Time [min]	Isolated yield [%][b])
		15	95
		90	94
		90	95

[a]) The structures of the products were established from their spectral (IR, ^{1}H- and ^{13}C-NMR, and MS) and analytical data and by comparision of the values with those reported earlier for the known compounds [6]. [b]) With respect to isolated material. [c]) The other regioisomer (*ca.* 5%) was also obtained.

After completion, the reaction was quenched with H_2O (10 ml), and the mixture was extracted with AcOEt (3×5 ml). The extract was concentrated and subjected to column chromatography (silica gel, hexane/AcOEt 9:1): pure β-(nitrooxy) alcohol or amine.

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