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Bismuth(III) Oxide Perchlorate Promoted Rearrangement of Epoxides to Aldehydes and Ketones

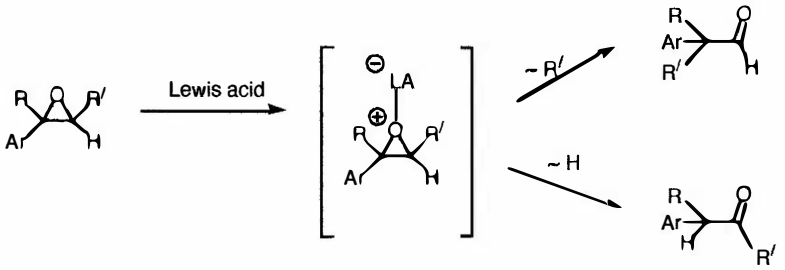
Andrew M. Anderson, Jesse M. Blazek, Parie Garg, Brian J. Payne and Ram S. Mohan

Abstract
Aryl-substituted epoxides and aliphatic epoxides with a tertiary epoxide carbon undergo smooth rearrangement in the presence of 10–50 mol% bismuth(III) oxide perchlorate, $BiOClO_4 \cdot xH_2O$, to give carbonyl compounds. The rearrangement is regioselective with aryl substituted epoxides and a single carbonyl compound arising from cleavage of benzylic C—O bond is formed. $BiOClO_4 \cdot xH_2O$ is relatively non-toxic, insensitive to air and inexpensive, making this catalyst an attractive alternative to more corrosive and toxic Lewis acids such as $BF_3 \cdot Et_2O$ or $InCl_3$ currently used to effect epoxide rearrangements.

Keywords: bismuth, bismuth compounds, epoxides, rearrangements.

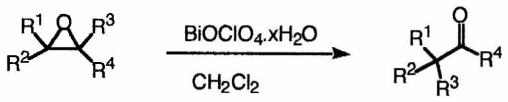
Epoxides are one of the most versatile functional groups in organic chemistry due to their ready availability and ease of transformation into a wide variety of functional groups.[1] The rearrangement of epoxides to carbonyl compounds is a useful synthetic transformation and several reagents have been utilized for this purpose. Some examples include $BF_3 \cdot Et_2O$,[2a] lithium salts,[2b] $MgBr_2$,[2a] and more recently, $Pd(OAc)_2$ in the presence of a phosphine ligand[2c] and $InCl_3$.[2d] The constitution of the rearrangement product is determined by the identity of the Lewis acid, the migratory aptitude of the epoxide substituents, and the solvent (Scheme 1).

Despite a number of methods that have been developed for this rearrangement, only a few are both regioselective and catalytic in nature. For example, $BF_3 \cdot Et_2O$ and $MgBr_2$ are typically used in stoichiometric or excess amounts.[2a] In addition, many of these reagents have some drawbacks. Boron trifluoride etherate is corrosive and air-sensitive while indium chloride is highly toxic and very expensive. The rearrangements promoted by these reagents also require anhydrous conditions. With increasing environmental concerns, it is imperative that new 'environment friendly' reagents be developed.[3] Recently, bismuth compounds have become attractive candidates for use as reagents in organic synthesis for several reasons. Most bismuth compounds are relatively non-toxic, readily available at low cost and are fairly insensitive to small amounts of water.[4] Bismuth has an electron configuration of



Scheme 1.

$[Xe]4f^{14}5d^{10}6s^26p^3$. Due to the weak shielding of the 4*f* electrons (Lanthanide contraction), bismuth(III) compounds exhibit Lewis acidity. The Lewis acidity of bismuth(III) chloride and bismuth triflate have been recently exploited in organic synthesis. They are catalysts for Diels–Alder,[5] Michael[6] and aldol reactions.[7] We wish to report that $BiOClO_4 \cdot \times H_2O$ is a very efficient reagent for rearrangement of epoxides to carbonyl compounds (Eq. (1), Table 1).



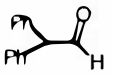
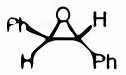
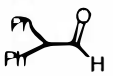
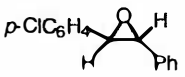
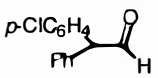
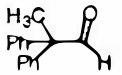
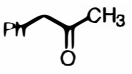
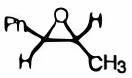
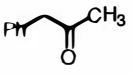
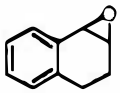
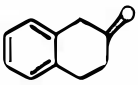
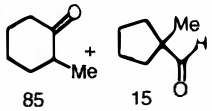
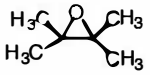
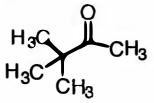
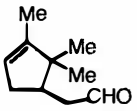
(1)

$BiOClO_4 \cdot \times H_2O$ is commercially available and requires no special handling.[8] Use of an inert atmosphere is not required unless the product is particularly air sensitive (entries 5–7). The reagent is insoluble in common organic solvents and is used as a suspension. For most epoxides, the best yields were obtained with use of 20 mol% reagent though stilbene oxides (entries 1–4) underwent smooth rearrangement with as little as 10 mol% reagent. Dichloromethane was found to be the best solvent for the rearrangement. The rearrangement was very slow in tetrahydrofuran and benzene while no rearrangement was observed when diethyl ether was used as the solvent.

Rearrangement of stilbene oxides (entries 1–4) gave only the diphenylacetaldehydes. Thus, this procedure is a good example of an epoxide rearrangement method that is both catalytic and regioselective in nature. These cases gave very clean products, and further purification was deemed unnecessary. In all cases, the phenyl group was found to migrate in preference to hydrogen. Thus, rearrangement of both *cis*- and *trans*-stilbene oxides (entries 1 and 2) gave diphenylacetaldehyde as the only product. In contrast, the rearrangement of *trans*-stilbene oxide by $MgBr_2$ in benzene gave a 3:1 mixture of diphenylacetaldehyde (phenyl migration) and deoxybenzoin (hydrogen migration).[2c] With $BF_3 \cdot Et_2O$, *trans*-stilbene oxide gives only diphenylacetaldehyde while the *cis* isomer gives a mixture of both diphenylacetaldehyde and deoxybenzoin. It was found that hydrogen migrates in preference to a methyl group: both *cis*- and *trans*-β-methylstyrene oxides (entries 5 and 6) gave only phenylacetone upon rearrangement.

Rearrangement of styrene oxide did not give a very pure product. While starting material was seen to disappear by TLC in 15 min, the crude product appeared to be very impure and attempted purification gave very low yields (15%) of phenylacetaldehyde. Contrary to reports in the literature,[2d] we were not able to repeat the rearrangement of styrene oxide with indium chloride in good yield. In our hands, styrene oxide rearranged rapidly, both with $InCl_3$ and $BiOClO_4 \cdot \times H_2O$ but the product phenylacetaldehyde was found to be unstable to the reaction conditions. A significant amount of product formed by aldol condensation of phenylacetaldehyde was detected in the crude product mixture. Aliphatic epoxides that contained a tertiary epoxide carbon also underwent rearrangement readily. For example, 1-methylcyclohexene oxide (entry 8) underwent ready rearrangement to give an 85:15 mixture of 2-methylcyclohexanone (migration of methyl group) and 1-methyl-1-cyclopentanecarboxaldehyde

Table 1
Rearrangement of epoxides with $BiOClO_4 \cdot \times H_2O$ in CH_2Cl_2

Entry[a]	Epoxide	Time[b]	Product	Yield (%)[c]
1[11]		25 min		90
2		45 min		90
3[12]		45 min		90
4[2d]		45 min		68
5		45 min		70
6		45 min		70
7		45 min		70
8[2b]		1 h	 85 15	71[d]
9[9]		1h		75[e]
10[10]		40 min		88

[a]Superscripts against entry # refer to literature reference for product. [b]All reactions were run at room temperature. [c]Yields refer to isolated, purified product. [d]The ketone:aldehyde ratio in the crude product mixture was determined by GC analysis to be 85:15, respectively. [e]Due to volatile nature of the product, the solvent was removed at atmospheric pressure using a water bath at 50 °C.

(migration of C–C bond), respectively. In contrast, rearrangement of 1-methylcyclohexene oxide with LiBr-HMPA in benzene gave 1-methyl-1-cyclopentanecarboxaldehyde as the major product (95%).[2b] Good yields of *tert*-butyl methyl ketone were obtained by rearrangement of the aliphatic epoxide 2,3-dimethylbutene oxide (entry 9).[9] The rearrangement of α-pinene oxide (entry 10) occurred quite readily at room temperature to give the expected aldehyde in good yield.[10] Cyclohexene oxide did not undergo rearrangement even when refluxed for 12 h and the starting material was recovered in good yield. This indicates that $BiOClO_4 \cdot \times H_2O$ is a mild Lewis acid. When cyclohexene oxide is reacted with $InCl_3$, while no rearrangement occurs, the corresponding chlorohydrin is reported to form in good yield.[2d]

In summary, this work demonstrates a new method for high-yielding, selective rearrangement of aromatic epoxides to carbonyl compounds using $BiOClO_4 \cdot \times H_2O$. Aliphatic epoxides containing a tertiary epoxide carbon also undergo facile rearrangement. Advantages of this method include low toxicity and low cost of the Lewis acid catalyst, fast reaction rates and insensitivity to air and moisture. A representative procedure is given here: A solution of *trans*-stilbene oxide (1.00 g, 5.10 mmol) in CH_2Cl_2 (20 mL) was stirred as $BiOClO_4 \cdot \times H_2O$ (0.331 g, 1.02 mmol) was added. After 25 min, water (10 mL) and CH_2Cl_2 (10 mL) were added and the organic layer was washed with 10% $NaHCO_3$ (10 mL) and saturated sodium chloride (10 mL). The organic layer was dried (Na_2SO_4) and the solvent was removed on a rotary evaporator to yield 0.879 g (88%) of diphenylacetaldehyde that was determined to be >98% pure by ^1H NMR.[11,12]

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