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Correction to Rearrangement Reactions of Lithiated Oxiranes

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The last statement of the first paragraph of the Introduction of ref 1 states that the reaction of 1,2-epoxy-5-hexene with lithium 2,2,6,6-tetramethylpiperidide (LTMP) leads to the aldehyde, presumably by the keto−enol isomerization of the vinyl alcohol. However, in 2004, Hodgson et al. reported that terminal epoxides in the presence of hindered lithium amides like LTMP formed the enamine almost exclusively by trapping of the lithiated epoxide by the lithium amide.[2] Detailed experimental evidence for this pathway was presented in later work.[3] Therefore, in the case of terminal aliphatic epoxides, the aldehyde is formed by the hydrolysis of the enamine. We sincerely regret our lack of awareness of these important reports at the time the paper was accepted and wish to correct our statement.

In contrast to the ring-opening considered in Scheme 2 of ref 1, which was at the β-carbon with respect to the deprotonated center, the α-ring-opening mechanism is also known. This latter pathway involves the formation of carbenes or carbenoids, leading to vinyl alcohols (and ketones) directly in certain cases[4,5] and allyl alcohols if the α-deprotonation is followed or accompanied by a 1,2 H-transfer.[6] Because our focus in ref 1 was on noncarbenoid rearrangements, we did not consider these reactions in our computations. At the same time, we regret that our Introduction failed to mention these possibilities and, therefore, conveyed an incomplete picture of the richness of oxirane rearrangement chemistry.

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