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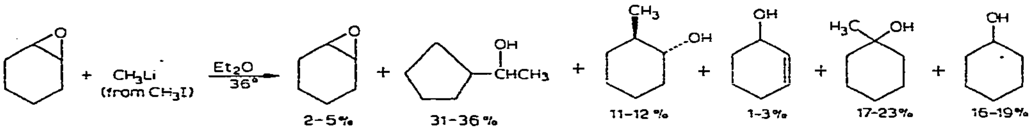
PRELIMINARY NOTE

The reaction of cyclohexene oxide with methyllithium

Several recent reports describe the marked effect of dissolved lithium halide on the course of reactions involving organolithium-generated carbenoid reagents[1,2]. We wish to report another example of the extreme effect of dissolved lithium halide on the course of a reaction employing an organolithium reagent.

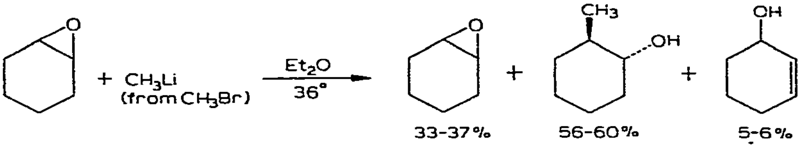
The reaction of cyclohexene oxide with methyllithium has been reported to give a mixture of *cis*- and *trans*-2-methylcyclohexanol in 63% yield[3]. We have found that the reaction is considerably more complex than this result would indicate and that the course of the reaction is strongly influenced by the halide from which the methyllithium is prepared.

When cyclohexene oxide was treated with methyllithium which was prepared from methyl iodide, (and which thus contained lithium iodide) a complex mixture of products resulted*:



(1)

On the other hand, treatment of cyclohexene oxide with methyllithium which was prepared from methyl bromide (and which thus contained lithium bromide) gave a much simpler product mixture:



(2)

These results suggested that the iodide anion was the cause of the complex mixture found in Reaction 1, and that addition of anhydrous lithium iodide to a reaction mixture composed of cyclohexene oxide and methyllithium (from methyl bromide) should result in a mixture of products similar to that found in Reaction 1. This was found to be the case:

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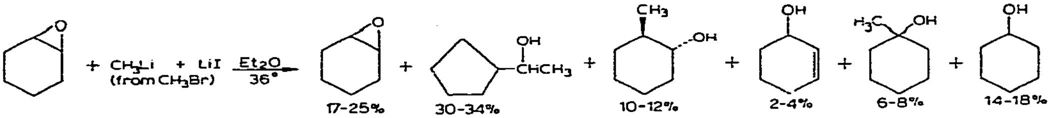
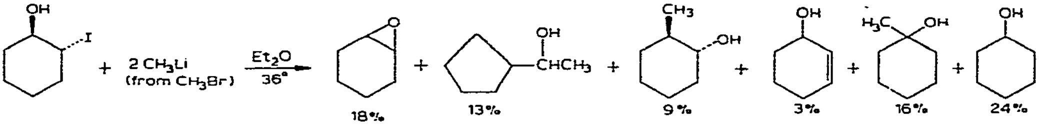
* All reactions were carried out under an atmosphere of dry nitrogen on a 100-mmole scale, using a 1 : 1-molar ratio of reactants, except Reaction 4 where a 1 : 2-molar ratio of reactants was used. Product mixtures were analyzed by gas chromatography using a combination of Silicone oil 550 and TCEP [1,2,3-tris(2-cyanoethoxy)propane] columns, or alternatively a combination of Carbowax 20 M and SE 30 columns, and using toluene as an internal standard. The cyclopentylmethylcarbinol and the *trans*-2-methylcyclohexanol were collected as a single peak (from the Silicone oil 550 column) and the mixture was analyzed by quantitative infrared spectrophotometry. All other products were isolated by gas chromatography and were identified by comparison of their infrared spectra with the spectra of authentic samples.



(3)

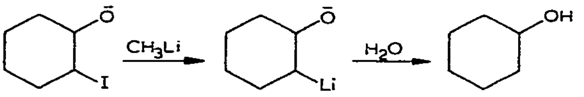
The formation of 2-substituted alkanols and allylic alcohols in reactions of base-nucleophiles with epoxides has been reported by several workers[3,4,5,6]. For a rationale of the formation of the other products, the corresponding Grignard reaction offers some analogies. For example, the principal product of the reaction of cyclohexene oxide with methyl Grignard reagent is cyclopentylmethylcarbinol[7]. There is ample evidence that this product is formed via the *trans*-2-halocyclohexanol and cyclopentanecarboxaldehyde[7,8,9]. It thus seemed likely that these two compounds were also intermediates in the reaction of cyclohexene oxide with methyllithium prepared from methyl iodide. Such is apparently the case. Treatment of cyclohexene oxide with anhydrous lithium iodide in ether gave *trans*-2-iodocyclohexanol, and treatment of the iodohydrin with methyllithium (from methyl bromide) gave a product mixture similar to those from Reactions 1 and 3:



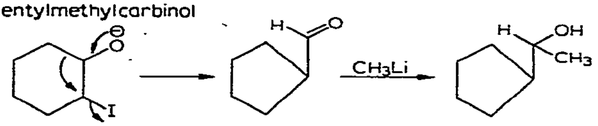
(4)

The "abnormal" products of the reaction of cyclohexene oxide and iodide-containing methyllithium may be rationalized as follows:

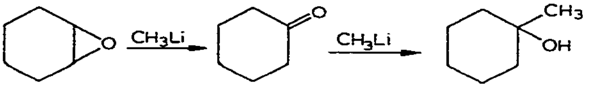
Cyclohexanol



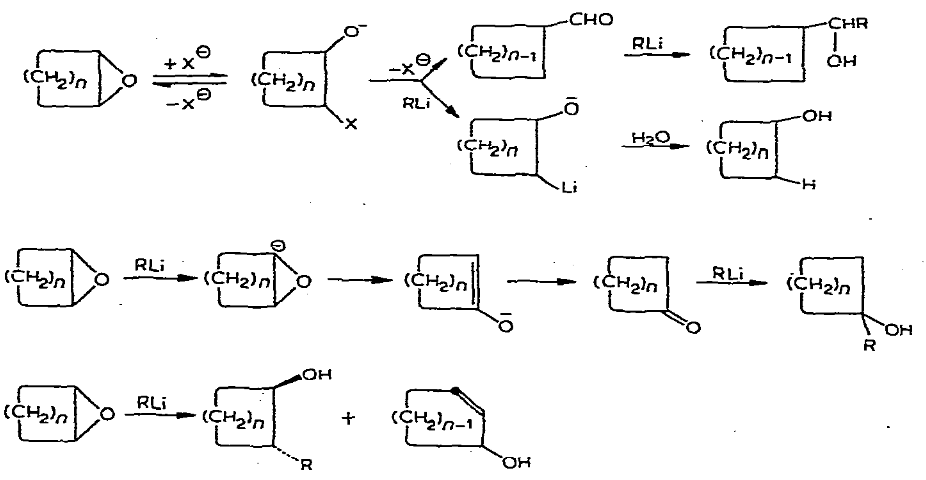
Cyclopentylmethylcarbinol



1-Methylcyclohexanol



On the bases of evidence now available, it seems possible that the course of the reaction of an epoxide with an alkyllithium compound in the presence of halide anion may be as follows:



Work which will indicate the generality of this scheme and also the course of the reaction of such epoxides with halide-free organolithium compounds is in progress.

Acknowledgement

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