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COPPER CATALYZED REDUCTIVE METALLATION OF A PROPARGYLIC EPOXIDE TO AN ALLENYL LITHIUM REAGENT

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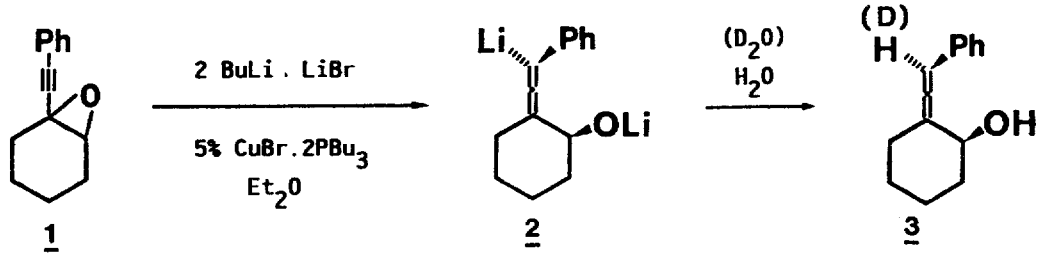
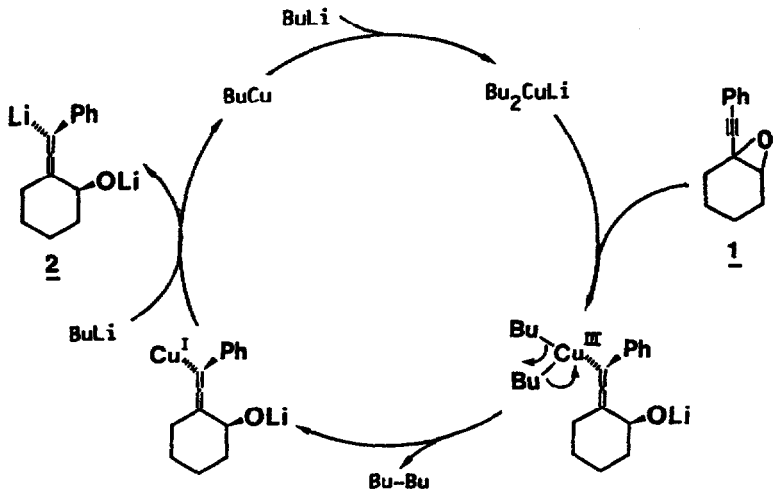
Summary : Phenethynyl cyclohexene oxide undergoes a reductive metallation by BuLi and catalytic amount of Cu^{I} salt. The resulting allenyl lithium reagent reacts, then, normally, with various electrophiles.

In the preceding letter[1] we have shown that Grignard reagents react with propargylic epoxides under copper^{I} catalysis to afford substituted allenols. Such copper^{I} catalyzed reactions are not usually performed with organolithium reagents[2]. We have already published a notable exception with allylic epoxides[3]. We report herein that in the case of phenethynyl cyclohexene oxide 1 the reaction takes an entirely different course from what we expected :

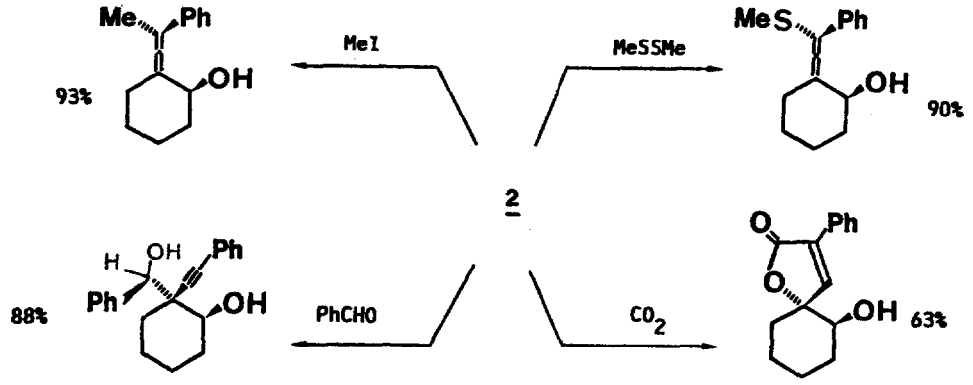


1 2 3

After hydrolysis, the allenol 3 was obtained quantitatively with 91% diastereoselectivity. That an intermediate organolithium reagent 2 was involved, was shown by deuteration with D_2O. Reduction products, such as 3, have already been obtained, in a similar reaction but with stoichiometric amounts of copper^{I} (R_2CuLi)[4]. Its formation was interpreted as a quench of an intermediate Cu^{III} organometallic[5]. In our case, where only 5% of copper^{I} salt is present, 2 has to be an organolithium reagent, whose formation may be accounted by the following catalytic cycle :



2 reacts normally and diastereoselectively, as an allenyl lithium reagent, with various electrophiles[6] (diastereomeric purity : $\geqslant$ 90%)



Noteworthy is the fact that the reagent 2 retains its stereochemistry during all the above transformations. The reaction cannot be performed without added Cu^I salts whatever the solvent. We are currently exploring the scope and limitations of this reaction.

Acknowledgments:

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References and notes :

1. A. Alexakis, I. Marek, P. Mangeney : Tetrahedron Lett., 30, 0000, (1989).
2. G.H. Posner : "An Introduction to synthesis using organocopper reagents", Wiley, New York, 1980.
3. G. Cahiez, A. Alexakis, J.F. Normant : Synthesis, 528 (1978).
4. P. Ortiz de Montellano : J. Chem. Soc., Chem. Comm., 709 (1973).
5. J.M. Dollat, J.L. Luche, P. Crabbé : J. Chem. Soc., Chem. Comm., 761 (1977).
6. All the products were fully characterized and their analytical and spectroscopic data will be reported soon in the full paper.

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