

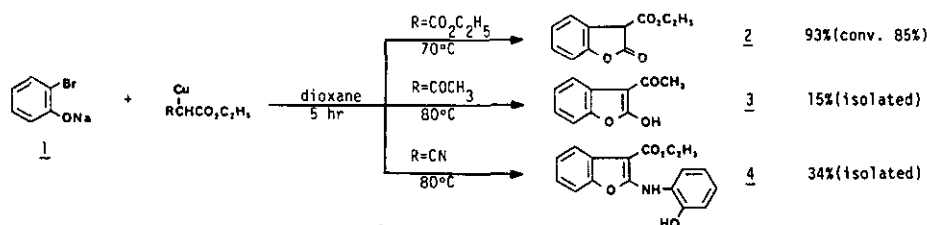
NOVEL SYNTHESIS OF BENZOFURAN AND CHROMAN DERIVATIVES

Kimihiro Matsukawa, Takashi Ueda, Jun-ichiro Setsune, and Teiji Kitao

Department of Applied Chemistry, College of Engineering, University of
Osaka Prefecture, Sakai, Osaka, 591

The aromatic nucleophilic substitution reaction is an intriguing alternative methodology in the synthesis of aromatic compounds, however the convenient methods of these reactions have not been accomplished. Recently, we have revealed that copper(I)-promoted nucleophilic substitution of various aryl halides with diethylmalonate anion proceeds effectively, even if aromatic nucleus is substituted with electron donating groups. We wish to report the novel synthesis of benzofuran and chroman derivatives via the coupling reaction of o-bromophenol derivatives with organocopper(I) complex of β -dicarbonyl compounds.

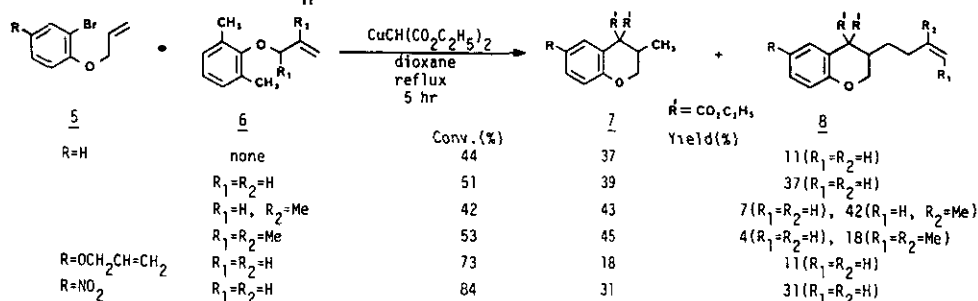
The reaction of sodium o-bromophenoxide **1** with organocopper(I) complex of β -dicarbonyl compounds afforded benzofuran derivatives **2**, **3**, and **4** respectively, as shown in Scheme 1. The



Scheme 1

formation of these products is explainable in terms of the initial substitution by the organo-copper(I) complexes followed by the intramolecular attack of the phenoxide anion to carbonyl or cyano group.

Chroman derivatives were prepared by the reaction of o-bromophenyl allyl ether **5** and copper(I) diethylmalonate, as shown in Scheme 2. Copper(I) complex of diethyl o-allyloxyphenylmalonate, the coupling product, cyclizes to give radical intermediate which abstracts hydrogen or allyl group from **5** or additive **6** by $\text{S}_\text{H} 2'$ type reaction.



Scheme 2