

Facile Synthesis of Various Ring-fused Alkylidene Derivatives and Their Electrochemical Reductions

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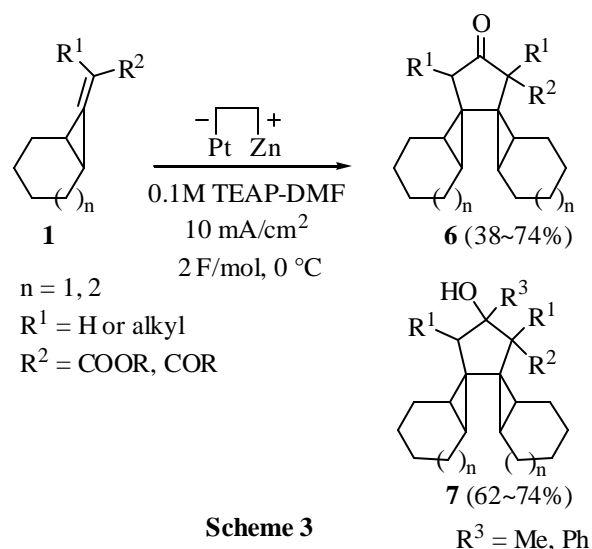
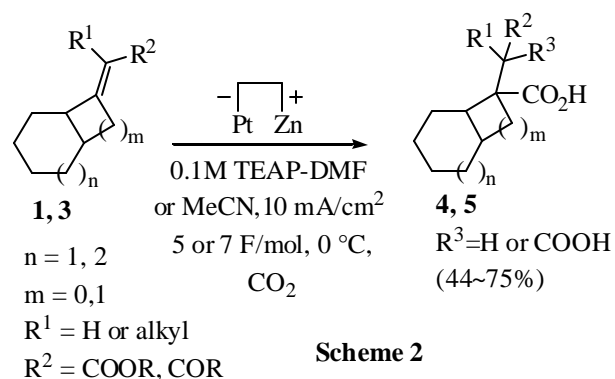
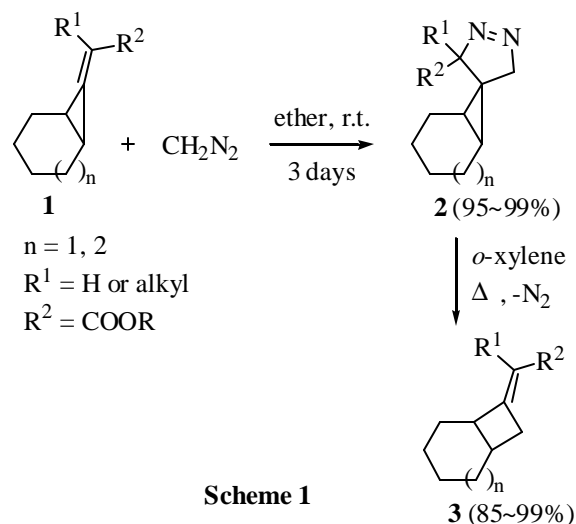
Methylenecyclopropane and its derivatives are very attractive and useful substrates in organic syntheses due to their unique reactivities originating from their highly strained structure. The release of strain energy associated with the cleavage of a cyclopropane ring in an organic molecule is able to bring about various transformations. Recently we reported a facile synthesis of ring-fused alkylidenecyclopropanes¹ and its derivatives² by olefination reaction of bicyclo[n.1.0]-alkanone *N,O*-hemiacetals with Wittig reagents. 1,3-Dipolar cycloaddition of diazomethane to ring-fused alkylidenecyclopropanes **1** gave spiro-pyrazolines **2** in 95~99% isolated yields. Thermal decomposition of these pyrazolines in *o*-xylene resulted in the cleavage of the cyclopropane ring which rearranged to ring-enlarged products alkylidenecyclobutanes **3** in 85~99% isolated yields (Scheme 1).

Electrochemical carboxylation is one of the most useful methods for the fixation of carbon dioxide to organic molecules because it is a clean and environmentally benign process. Carbon dioxide is non-toxic and can work as an electrophile in the reaction of anion species to give carboxylic acids with one carbon elongation. As an extension of our studies on electrochemical carboxylations,³ we recently carried out the electrochemical carboxylation of various ring-fused alkylidene derivatives prepared by our process, and wish to report here the results. Electrolysis of a system containing both atmospheric pressure of carbon dioxide and ring-fused alkylidene derivatives **1** and **3** was carried out in a one compartment electrochemical cell using a platinum plate cathode (2 x 3 cm²) and a zinc plate anode (2 x 3 cm²) in a suitable aprotic solvent such as DMF or MeCN. It is possible to achieve either a direct synthesis of a mono- or dicarboxylic acids **4** or **5** in 44~75% isolated yields (Scheme 2). In all cases tetraethylammonium perchlorate (TEAP) was used as a supporting electrolyte. Ring-fused alkylidenecyclopropanes **1** required 5 F/mole of electricity whereas ring-fused alkylidenecyclobutanes **3** required 7 F/mole of electricity and in both cases constant current density of 10 mA/cm² was used at 0 °C.

Electrochemical reductive coupling has been used as a synthetic tool for a variety of poly functional compounds.⁴ We also carried out some electrochemical reduction reactions of the prepared olefins **1** in the absence of CO₂ under the same electrolytic conditions as those of the carboxylations (Scheme 3). In case of esters we isolated spiro type compounds such as **6** in the yield of 38~74% and, in case of ketones, we also isolated spiro type compounds such as **7** in 62~74% yields.

ACKNOWLEDGMENTS

The authors acknowledge financial support from the Japan Society for the Promotion of Science (JSPS). M.A.C. is also grateful to JSPS for giving him a postdoctoral fellowship.



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