

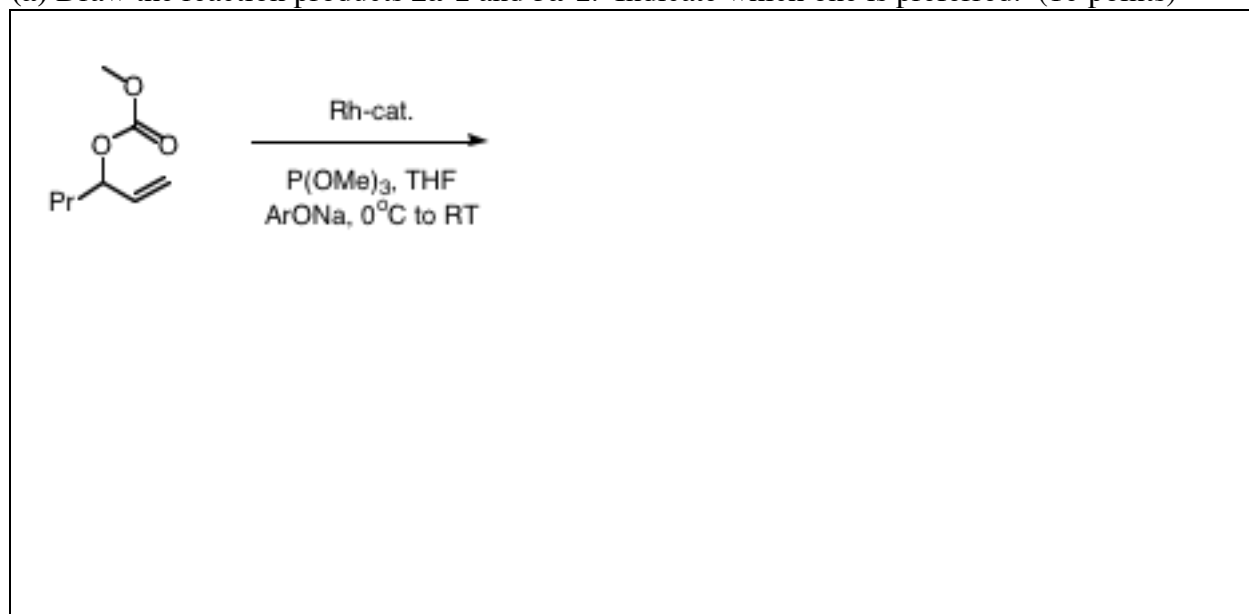
Regioselective and Enantiospecific Rhodium-Catalyzed Intermolecular Allylic Etherification with Ortho-Substituted Phenols

P. Andrew Evans and David K. Leahy

J. Am. Chem. Soc., **122** (20), 5012 -5013, 2000.

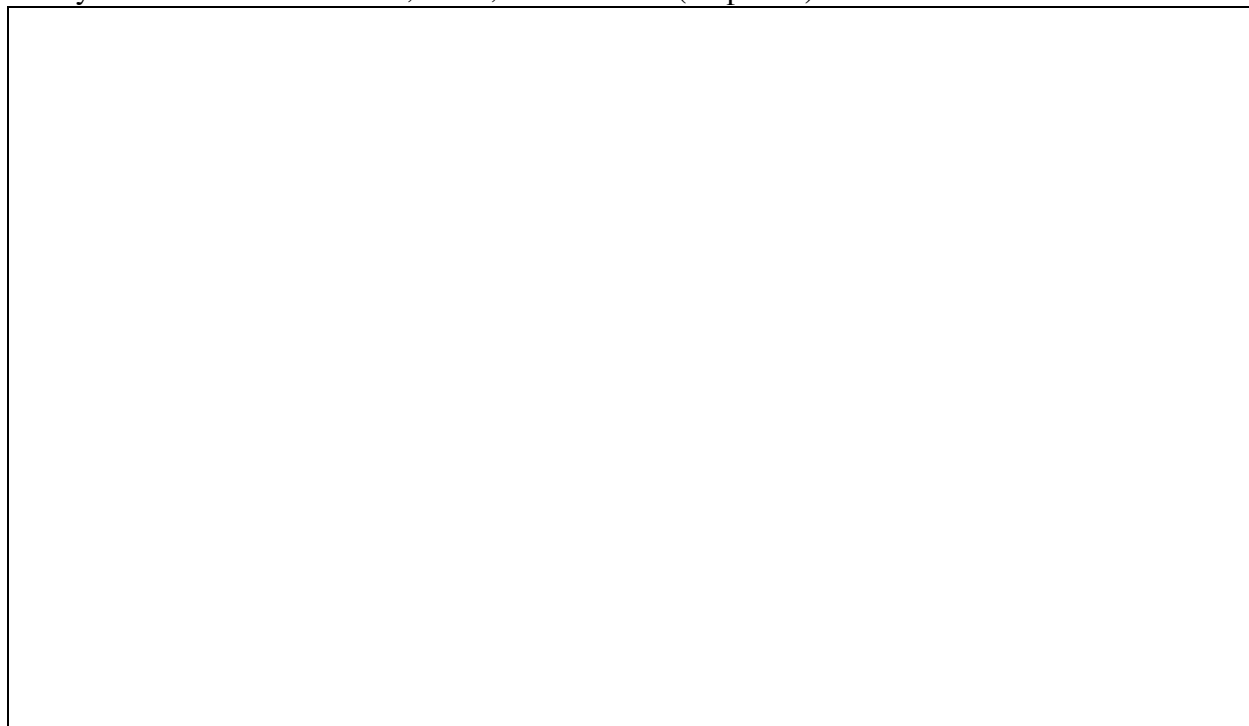
... In a program directed toward controlling regioselectivity in metal-catalyzed allylic substitution reactions, we have recently demonstrated that the rhodium-catalyzed reactions proceed with excellent selectivity. Herein, we describe the first rhodium-catalyzed allylic etherification reaction using the sodium salt of ortho-substituted phenols to afford the aryl allyl ethers **2/3a-1** in excellent yield, favoring the secondary derivative **2** (eq 1). The ability to utilize highly substituted phenols in this manner is expected to provide a useful cross-coupling reaction for organic synthesis. ...

(a) Draw the reaction products **2a-1** and **3a-1**. Indicate which one is preferred. (10 points)

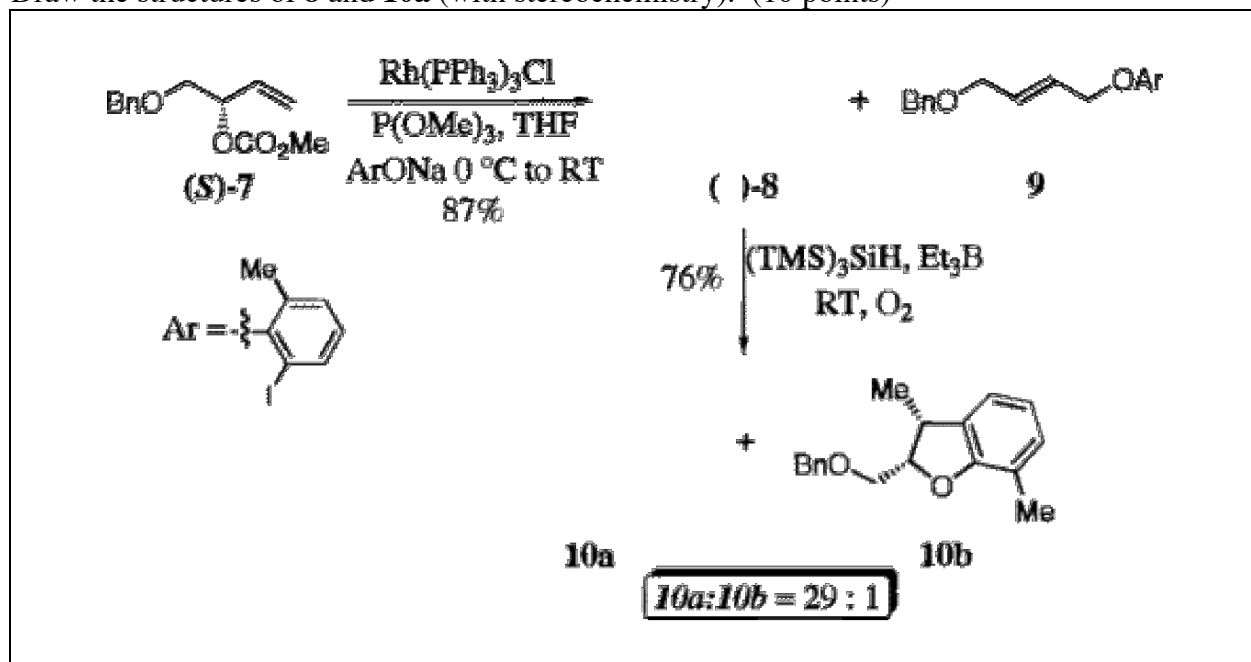


(b) What Rh-catalyst is employed? Name? Structure? Oxidation state of Rh? (5 points)

(c) Show the substrates that would be needed for the preparation of the aryl ether generated as the major product in (a) by way of a simple Williamson ether synthesis. Comment as to whether this synthesis would work well, so-so, or not at all. (10 points)



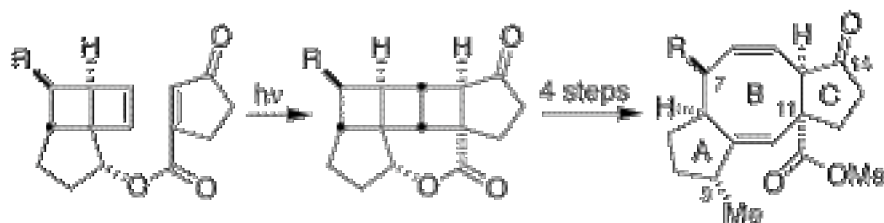
(d) The enantiospecific rhodium-catalyzed etherification was employed in a two-step sequence for the preparation of enantiomerically enriched oxygen containing heterocycles (Scheme 1). Draw the structures of **8** and **10a** (with stereochemistry). (10 points)



Intramolecular [2 + 2]- Photocycloaddition/Thermal Fragmentation Approach toward 5-8-5 Ring Systems

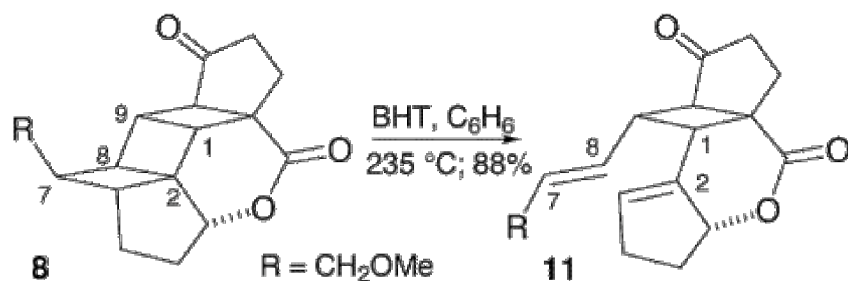
Priscilla C.-K. Lo and Marc L. Snapper

Org. Lett., **3** (18), 2819 -2821, 2001.

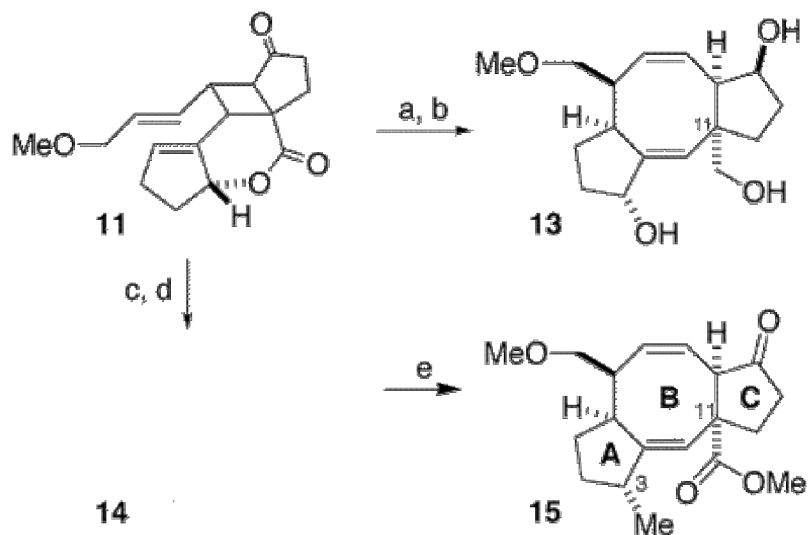


Abstract: An intramolecular [2 + 2]-photocycloaddition is used to provide a photoadduct, which upon fragmentation, lactone cleavage, and subsequent Cope rearrangement provides a dicyclopenta[*a,d*]cyclooctene ring system with substituents in place (e.g., C3 and C11) to access several 5-8-5 diterpene and sesterterpene natural products.

(a) Thermolysis of photoadduct **8** was carried out at 235 °C in benzene (Scheme 4). Instead of generating *cis,trans*-1,5-cyclooctadiene **12**, the thermodynamically more favored dialkenyl cyclobutane **11** was produced in 88% yield. Explain the mechanism. (4 points)

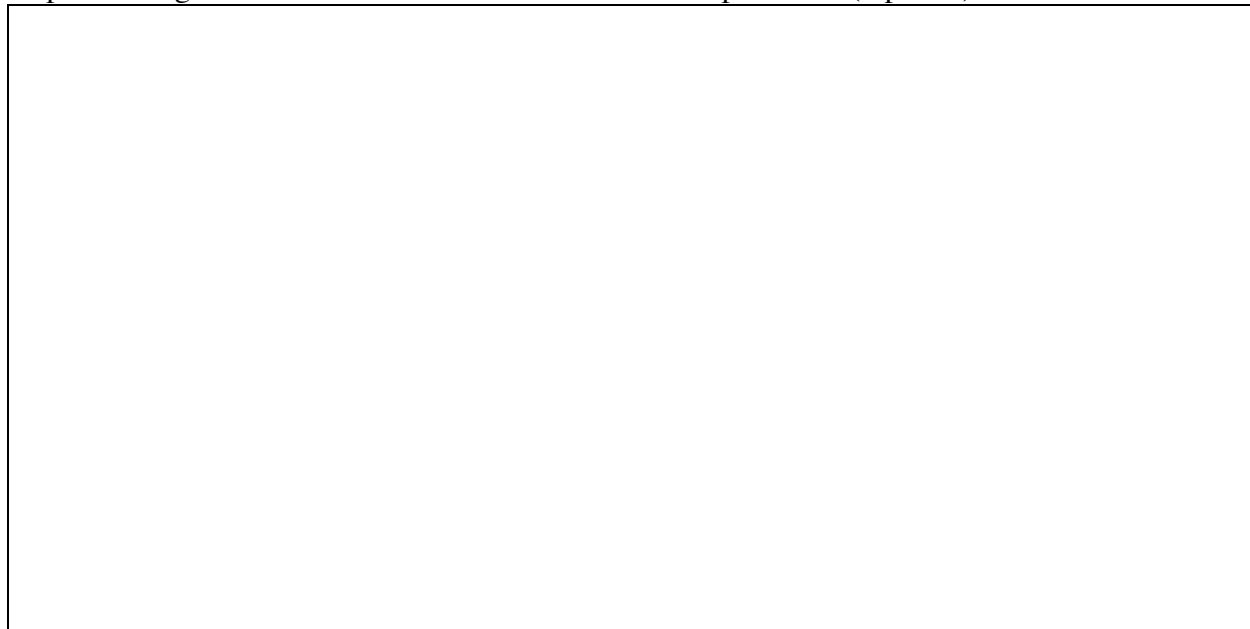


(b) Draw the structure of **14** and show how it is formed from **11**. Note that **14** is converted into **15** by Cope rearrangement. (16 points)

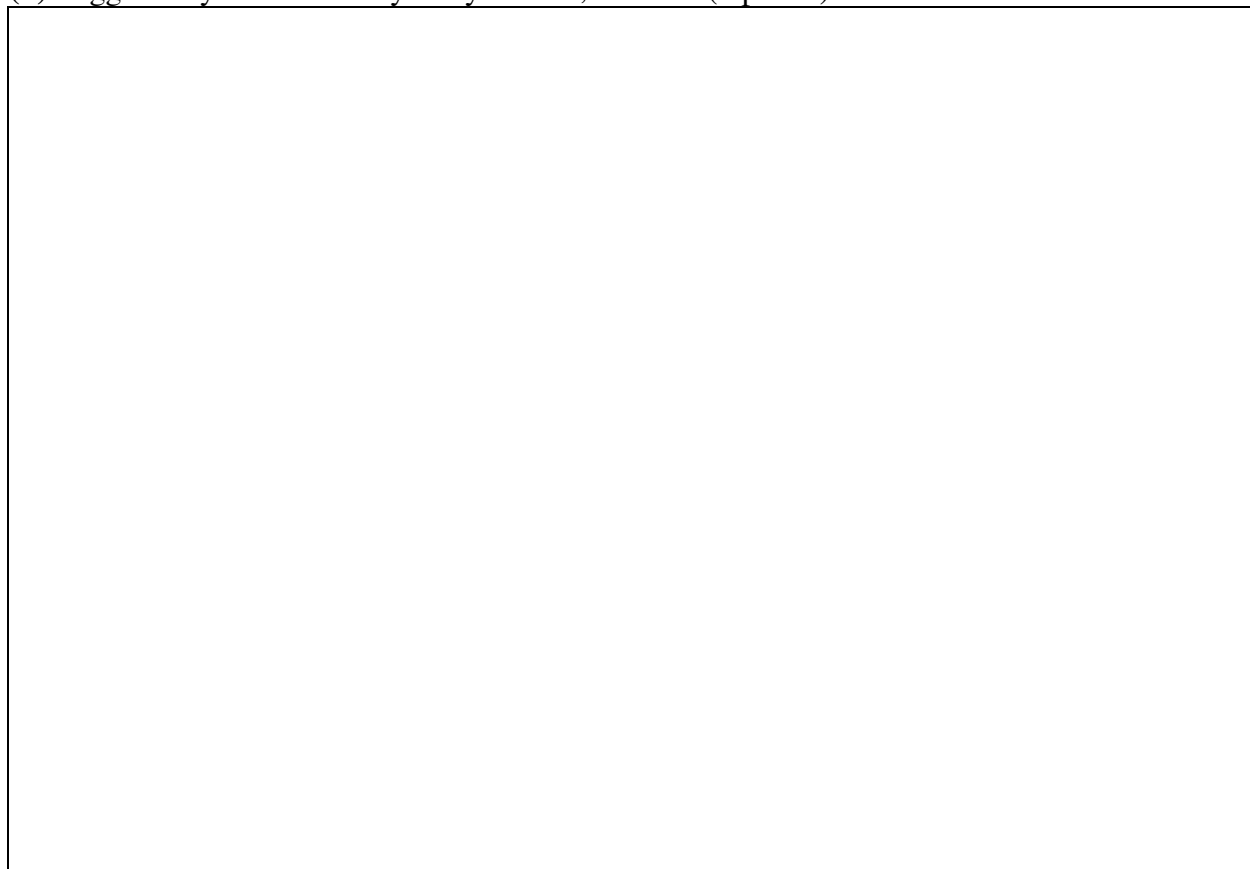


(a) LiAlH_4 , 53%; (b) C_6H_6 , 140 °C, 94%; (c) MeMgBr , $\text{CuBr}\cdot\text{Me}_2\text{S}$, Me_2S , THF, -20 °C; **11**, 66% **14**:1 dr; (d) TMSCHN_2 , MeOH/PhH, r.t., 93%; (e) C_6H_6 , BHT, 120 °C, 96%.

(c) Consider the Cope rearrangement of 3-hydroxy-hexa-1,5-diene. What is the product of the Cope rearrangement? What is the structure of the final product? (6 points)



(d) Suggest a synthesis of 3-hydroxy-hexa-1,5-diene. (9 points)



Ring Strain. The Snapper reactions rely on the relief of ring strain and the provides an opportunity to some of the basics of ring strain. The following questions are addressed in any standard textbook.

(a) Cyclopropane has a total ring strain energy of 28 kcal/mol. Explain in some detail how this number is determined. What measurements have to be done? What kind of “work-up” of the numbers needs to be done? (14 points)

(b) The heats of combustion of ethylcyclopropane and of methylcyclobutane have been measured as 801.2 and 808.8 kcal/mol, respectively. Assign the correct heat of combustion to each isomer. (8 points).

(c) [14]Annulene is strained while [18]annulene is not. Explain this finding. (8 points)

