Theoretical and Physical Organic Chemistry
Homework II

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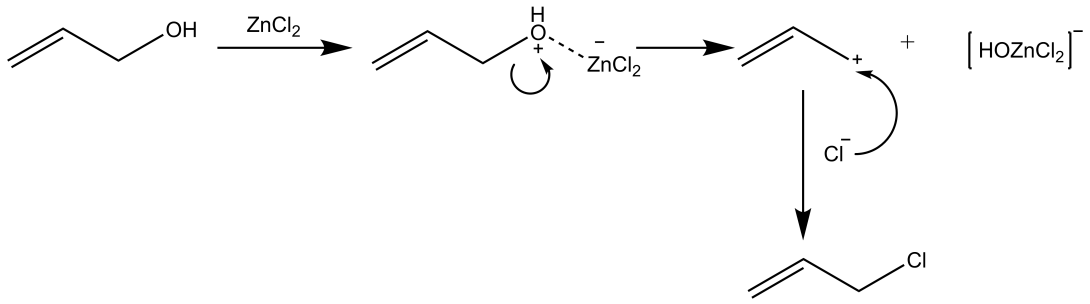
1

A.

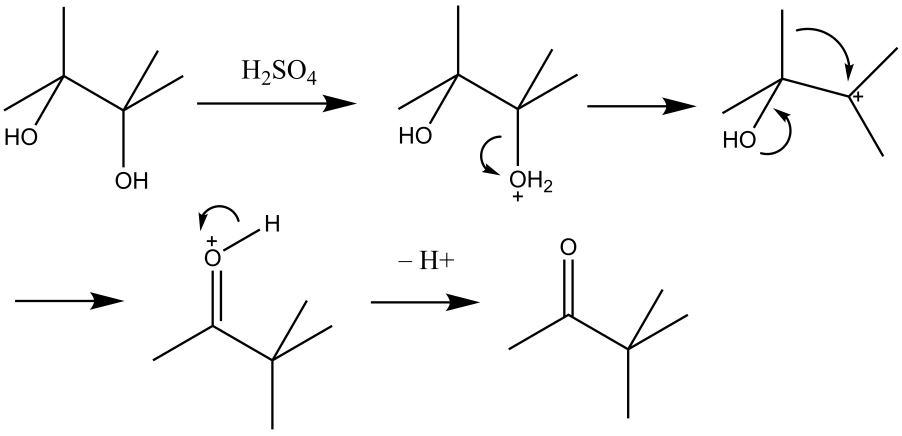
S_NI reaction with Lucas reagent (last step)



Lucas, H. J. *J. Am. Chem. Soc.* **1930**, *52*, 802–804, DOI: 10.1021/ja01365a053

B.

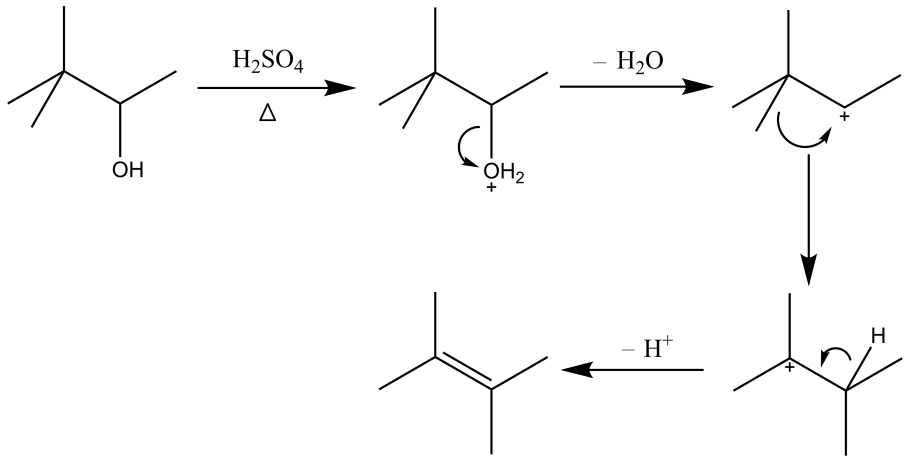
pinacol rearrangement (last step)



Fittig, R. *Justus Liebigs Annalen der Chemie* **1859**, *110*, 17–23, DOI: 10.1002/jlac.18591100103

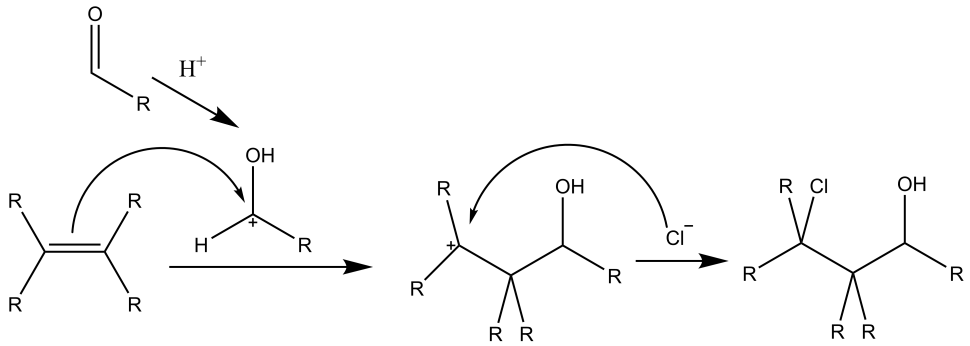
C.

Wagner-Meerwein rearrangement



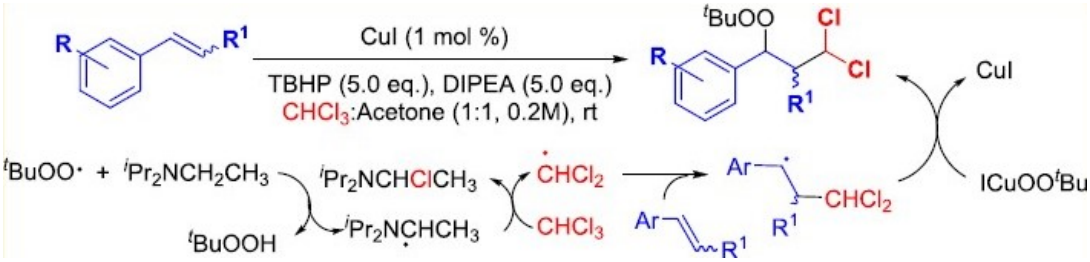
D.

Prins reaction



2

A. Generation of Halomethyl Radicals by Halogen Atom Abstraction and Their Addition Reactions with Alkenes

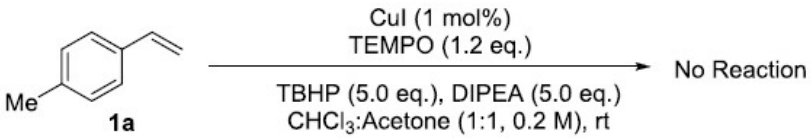


Neff, R. K. et al. *J. Am. Chem. Soc.* **2019**, *141*, 16643–16650, DOI: 10.1021/jacs.9b05921

Generation of radicals
Using *t*–BuOO· to generate ·$CHCl_2$, where *t*–BuOO· is generated by the reaction of *t*–BuOOH(TBHP) and CuI.

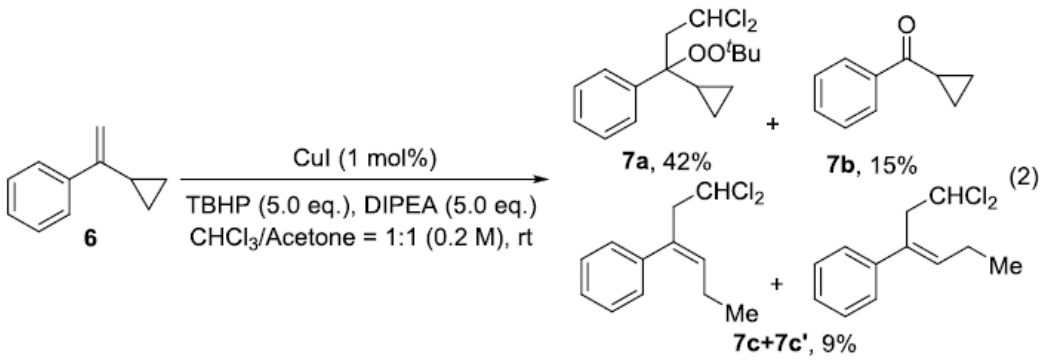
Proof of the radical mechanism

- TEMPO trapping experiment



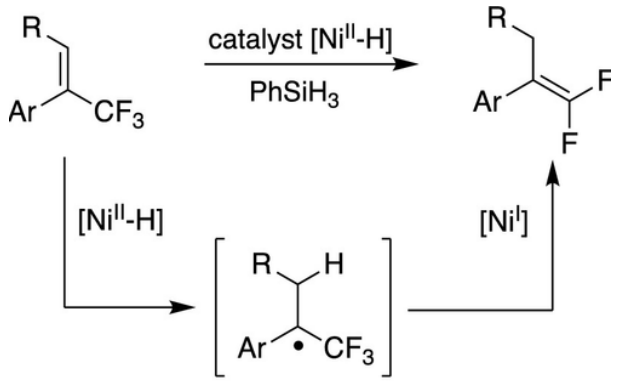
(1)

- Mechanistic experiment with vinylcyclopropane



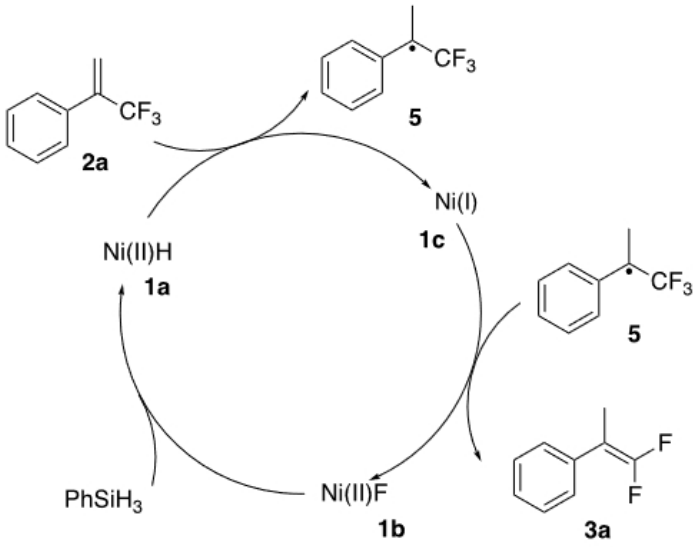
(2)

B. Catalyzing the Hydrodefluorination of CF_3-Substituted Alkenes by $PhSiH_3$. H· Transfer from a Nickel Hydride



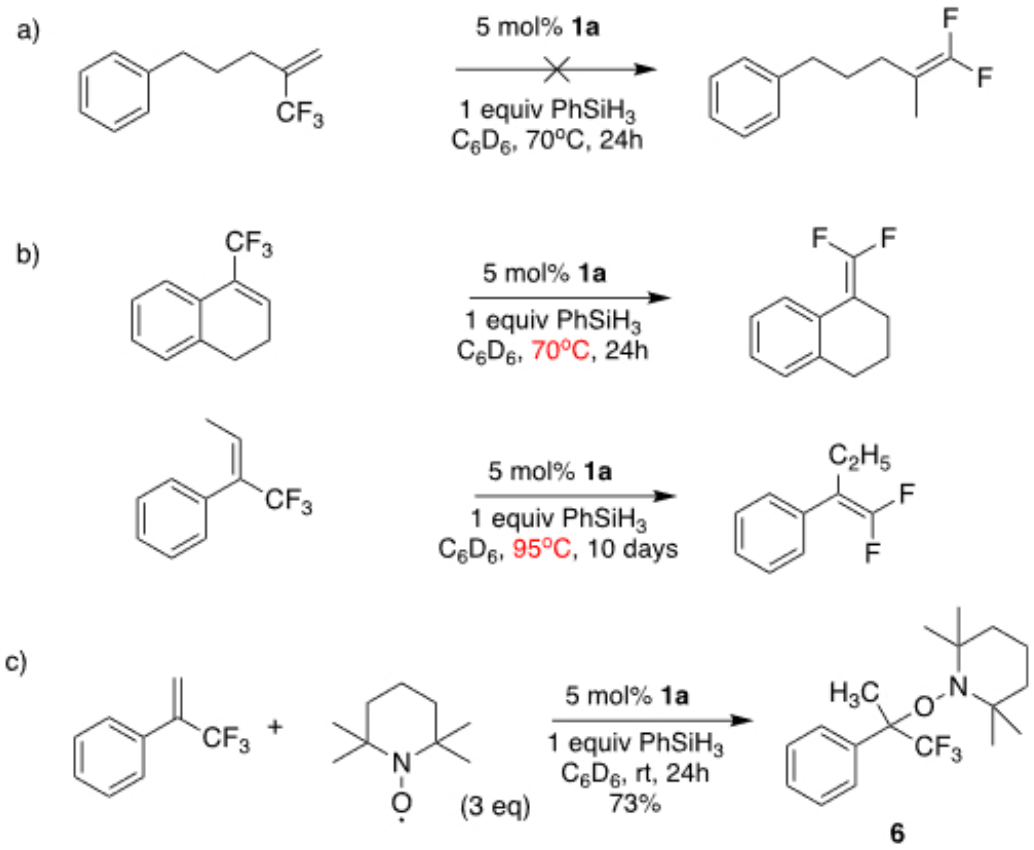
Yao, C. et al. *J. Am. Chem. Soc.* **2020**, *0*, null, DOI: 10.1021/jacs.9b13757

Generation of radicals



Radical is initiated by H· transfer from nickel hydride.

Proof of the radical mechanism



- a) Aliphatic alkenes do not work even at an elevated temperature. Aryl group is essential for stabilizing the organic radical resulting from HAT (Hydrogen Atom Transfer), compared with another possible mechanism (Fluorine Atom Abstraction).
- b) Methyl substituent on the carbon receiving the H·(in the second mechanism) is known to slow HAT, while should not affect another mechanism.
- c) TEMPO trapping experiment