Exercise Session

Problem:

Questions:

- ➤ What is the compound **14**?
- \triangleright Write the mechanism for the step **c**.
- ➤ What is the missing reagent, which will provide the formation of 1,3-diketone **16**? Use retrosynthetic analysis to predict this reagent. How can you synthesize it?
- \triangleright Give the mechanisms for both steps (**f** and **g**) in transformation **16** to **27**.
- > Suggest 5 steps for transformation 27 to 29.
- ➤ What is the final product 2? What is the name of first reaction?

Annulative Methods Enable a Total Synthesis of the Complex Meroterpene Berkeleyone A

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1. Compound **14**.

14

2. Mechanism of step c.

$$2 Cp_2TiCl_2 + Zn = 2 Cp_2TiCl + ZnCl_2$$

- Scheme 2 Reaction mechanism of Cp₂TiCl with epoxynitriles
- A. Fernández-Mateos, et al. *Synlett* 2004, *6*, 1011 1014.
- A. Fernández-Mateos, et al. Synlett 2007, 17, 2718 2722.

3. Missing reagent and ways of synthesis of diketene and ketene.

OLi
$$R_1$$
 R_2
 R_3
 R_3
 R_2
 R_3
 R_2
 R_3
 R_3
 R_2
 R_3
 R_3
 R_4
 R_2
 R_3

Wolff Rearrangement

$$\begin{array}{c} \text{Wolff rearrangement} \\ \text{No} \\ \text{No} \\ \text{diazoketone} \end{array} \begin{array}{c} \text{Wolff rearrangement} \\ \text{No} \\$$

Dehydrohalogenation of acyl chlorides or pyroliz of acetone

4. Mechanisms for both steps (f and g) in transformation 16 to 27.

5. 5 steps for transformation **27** to **29**. Final product **2**. Krapcho-type demethylation.

