Total Synthesis of Rubriflordilactone B.¹ Main block of this compound + Bonus²!



- ▶ What are the name and the mechanism for modified well-known reaction 11 to 16?
- Step from 16 to 17 include actually two subsequent reactions. One of them is a name reaction. Give the mechanism for whole transformation.
- What is the product 9? What is the name for first reaction from 17 to 9 (first letter "M" last letter "a")? Give the mechanism for this reaction.
- Give the mechanism for the transformation from 19 to 20. Different type of reaction, but it has name from the same human as last reaction before. Why treatment with strong aqueous acid was not the best solution?
- \blacktriangleright Give the mechanism for second step of transformation 20 to 8. What is the name for reagent 2?
- What are the products 23 and 6? What is the famous reaction in transformation 23 to 24? Which reaction is using for alcohol deoxygenation in radical chemistry? Give mechanisms.

Bonus:

Problem:



What is the name of the last reaction? Propose the mechanism for this good alternative for Wittig reaction.

¹ P. Yang, M. Yao, J. Li, Y. Li, A. Li Angew. Chem. Int. Ed. 2016, 55, 1-6.

² H. Fuwa, N. Yamagata, Y. Okuaki, Y. Ogata, A. Saito, M. Sasaki Chem. Eur. J. 2016, 22, 1-16.

Solution:

Problem I:

Arbuzov Reaction



M. Fernandez-Valle, R. Martínez-Álvarez, D. Molero-Vílchez, Z. Pardo, E. Saez-Barajas, A. Herrera J. Org. Chem. 2015, 80, 799-805.

Problem II:



The ozonolysis preferentially cleaved the trisubstituted C=C bond, presumably owing to electronic effects.

Horner-Wadsworth-Emmons Reaction



From http://www.organic-chemistry.org

Problem III:





From http://www.chem-station.com

Problem IV:

Mukaiyama hydration





Notably, treatment of 19 with strong aqueous acid directly delivered 20, presumably through olefin hydration–cyclization as well. However, the enantiopurity of the obtained product was significantly lower; a plausible mechanism is that the tertiary carbocation reversibly migrated to the neighboring carbon atom and thus lost the stereochemical information inherited from the chiral pool.

Problem V:

Davis oxaziridine

Davis oxidation (hydroxylation)



From http://www.chem-station.com

Problem VI:



Dieckmann Condensation

Barton-McCombie Reaction

R = Alkyl, R' = H, CH₃, SCH₃, OCH₃ Ph, OPh, Imidazolyl



From http://www.organic-chemistry.org

Bonus:



From https://en.wikipedia.org