Stereoselective Synthesis of Trisubstituted Alkenes via Intermolecular Olefin Metathesis

**Significance:** Crossed olefin metathesis is a challenge in organic chemistry because of the prevalence of side reactions from homo-metathesis. Hoveyda and co-workers report a crossed metathesis with high E/Z-selectivity generating trisubstituted haloalkenes. The reaction shows good to excellent E/Z-selectivity and can generate either the E or Z product depending on the stereochemistry of the starting olefin.

**Comment:** Alkenyl chloride products could be generated in good to excellent yields wherein the trans product was formed with higher E/Z ratios. Additionally, the alkenyl bromide products could be generated. The improved selectivity for the trans-olefin starting material was explained with the stereochemical model. In the case of the Z-olefin, the energy gap between the two potential pathways is less because steric repulsion is significant in both pathways, leading to lower E/Z ratios.

**Selected examples:**

- Mo-2 (5 mol%) 56% yield, E/Z = 94:6
- Mo-2 (10 mol%) 86% yield, E/Z = 95:5
- Mo-1 (5 mol%) 87% yield, E/Z > 98:2
- Mo-1 (5 mol%) 65% yield, E/Z = 21:79

**Additional examples:**

- PhBr, 22 °C, 4 h
  - Mo-2 (1 mol%) 66% yield, E/Z = 5:95
  - PhBr, 22 °C, 4 h
    - Mo-2 (1 mol%) 90% yield, E/Z > 98:2

**Stereochemical model:**

**Category**
- Metal-Catalyzed
- Asymmetric
- Synthesis and Stereoselective Reactions

**Key words**
- olefin metathesis
- molybdenum catalysis
- alkenyl halides

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**Synfacts 2018, 14(03), 0261 Published online: 15.02.2018**

**DOI:** 10.1055/s-0037-1609296; **Reg-No.:** L01118SF ©Georg Thieme Verlag Stuttgart · New York