SYNFACTS

Highlights in Current
Synthetic Organic
Chemistry

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Category

Metal-Mediated Synthesis

Key words

zinc

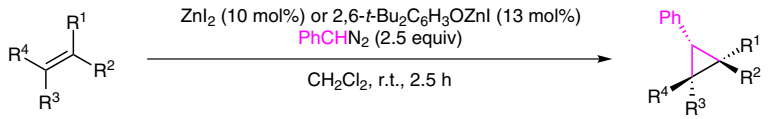
Simmons–Smith reaction

cyclopropanes

É. LÉVESQUE, S. R. GOUDREAU, A. B. CHARETTE* (UNIVERSITY OF MONTRÉAL, CANADA)

Improved Zinc-Catalyzed Simmons–Smith Reaction: Access to Various 1,2,3-Trisubstituted Cyclopropanes
Org. Lett. **2014**, *16*, 1490–1493.

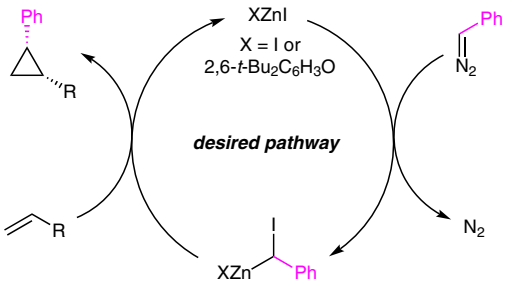
Synthesis of Phenylcyclopropanes from Allylic Alcohols



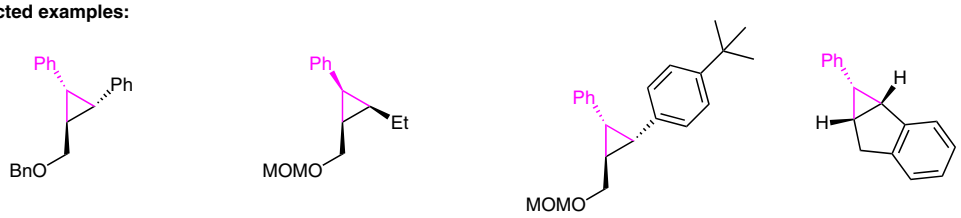
R^1, R^2 = H, Alk, Ar
R^3 = H, Me, CH_2OH, CH_2OBn, CH_2OMe, CH_2OMOM, CH_2OPv
R^4 = H, Me

up to 94% yield
dr up to >95:5

Proposed catalytic cycle:



Selected examples:

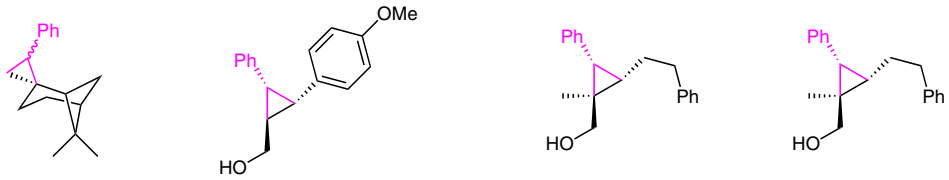


83% yield
dr > 95:5

69% yield
dr = 57:43

66% yield
dr = 92:8

65% yield
dr > 95:5



28%
dr = 50:50

85% yield
dr = 88:12

72% yield
dr > 95:5

86% yield
dr = 73:27

Significance: Charette and co-workers present an improved zinc-catalyzed Simmons–Smith reaction for the conversion of allylic ethers and styrenes into various phenylcyclopropanes in up to 94% yield and good diastereoselectivity.

Comment: The proposed mechanism for this reaction, which was reported earlier by this group, involves the generation of an iodo(phenyl)methylzinc carbenoid via double nucleophilic displacement between phenyldiazomethane and the catalyst XZnI.

SYNFACTS Contributors: Paul Knochel, Diana Haas
Synfacts 2014, 10(6), 0626 Published online: 16.05.2014
DOI: 10.1055/s-0033-1341292; **Reg-No.:** P05514SF

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