A. VOITURIEZ, L. E. ZIMMER, A. B. CHARETTE* (UNIVERSITÉ DE MONTRÉAL, CANADA)

Preparation of a Storable Zinc Carbenoid Species and its Application in Cyclopropanation, Chain Extension, and [2,3]-Sigmatropic Rearrangement Reactions
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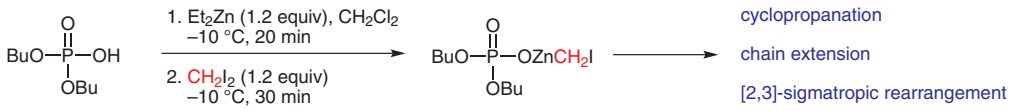
Category

Metal-Mediated Synthesis

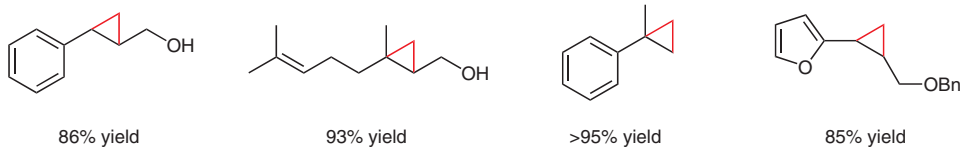
Key words

zinc carbenoids
cyclopropanation
chain extension
[2,3]-sigmatropic rearrangement

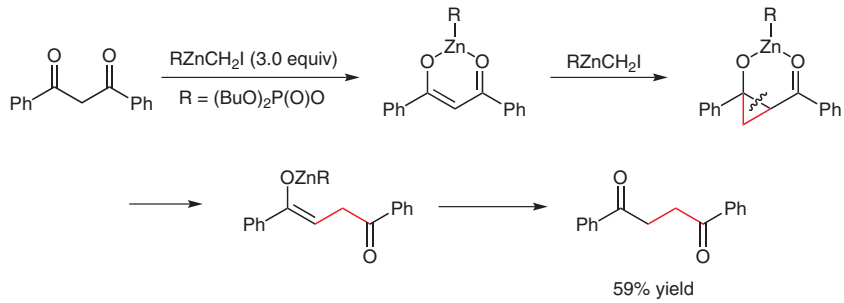
A New Phosphate Zinc Carbenoid



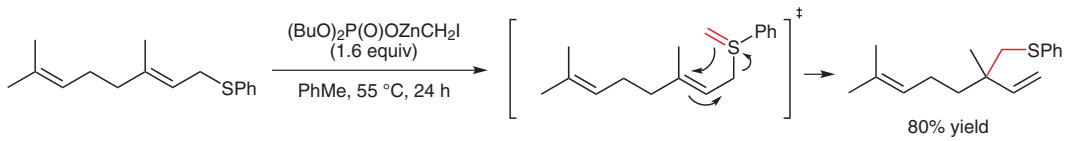
Examples for cyclopropanation reactions:
Conditions: 0.5–0.8 equiv of alkene, CH_2Cl_2, –10 °C to r.t., 20 h



Proposed mechanism for the chain extension of 1,3-diketones:



[2,3]-Sigmatropic rearrangement of sulfonium ylides:



Significance: $(BuO)_2P(O)OZnCH_2I$, a new phosphate carbenoid, shows very slow degradation at –22 °C and can be used several weeks after its synthesis. It is shown to be a powerful cyclopropanating agent for protected and unprotected allylic alcohols as well as styrenes or unfunctionalized alkenes. Good results are also obtained for the chain extension of 1,3-diketones and for the [2,3]-sigmatropic rearrangement of allylic sulfides.

Comment: Even after a period of six days at –22 °C, the phosphate carbenoid is still highly effective and cyclopropanations can be conducted in up to 97% yield. After 18 days, only a slight excess is needed to compensate for the slow degradation. To date, this is the first example of a storable carbenoid in solution. It would be very interesting to evaluate its efficiency in asymmetric synthesis.

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