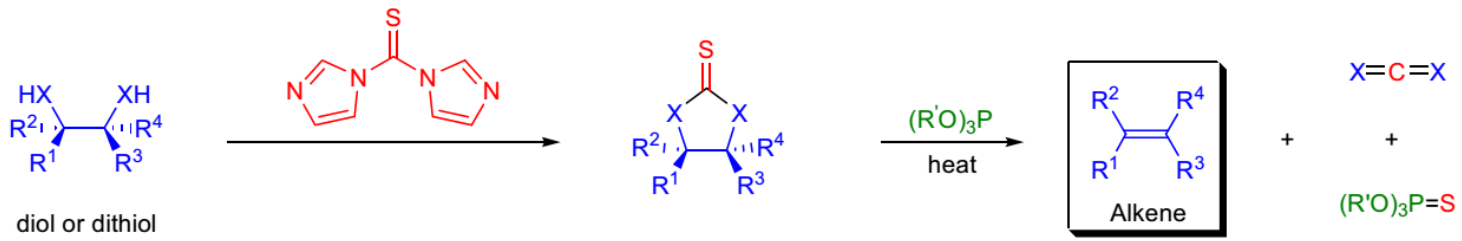
COREY-WINTER OLEFINATION

-By E.J. Corey and R.A.E. Winter



R^1, R^2, R^3, R^4 = H, alkyl, aryl; R' = Me, Et; substrate: X = O (1,2-diol), X = S, 1,2-dithiol;
cyclic intermediate: X = O (cyclic 1,2-thionocarbonate), X = S (cyclic 1,2-trithiocarbonate)

Abstract

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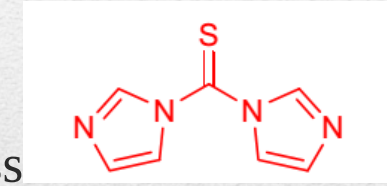
In 1963, E.J. Corey and R.A.E. Winter described a new two-step method for the stereospecific synthesis of alkenes from 1,2-diols via cyclic 1,2-thionocarbonates and 1,2-trithiocarbonates. This method of alkene synthesis is called the **Corey-Winter olefination.**

In the first step, the 1,2-diol is converted quantitatively to the corresponding cyclic thionocarbonate derivative using thiocarbonyldiimidazole

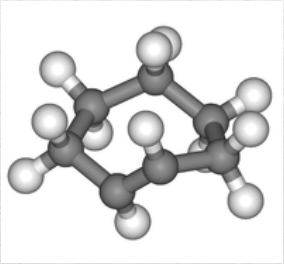


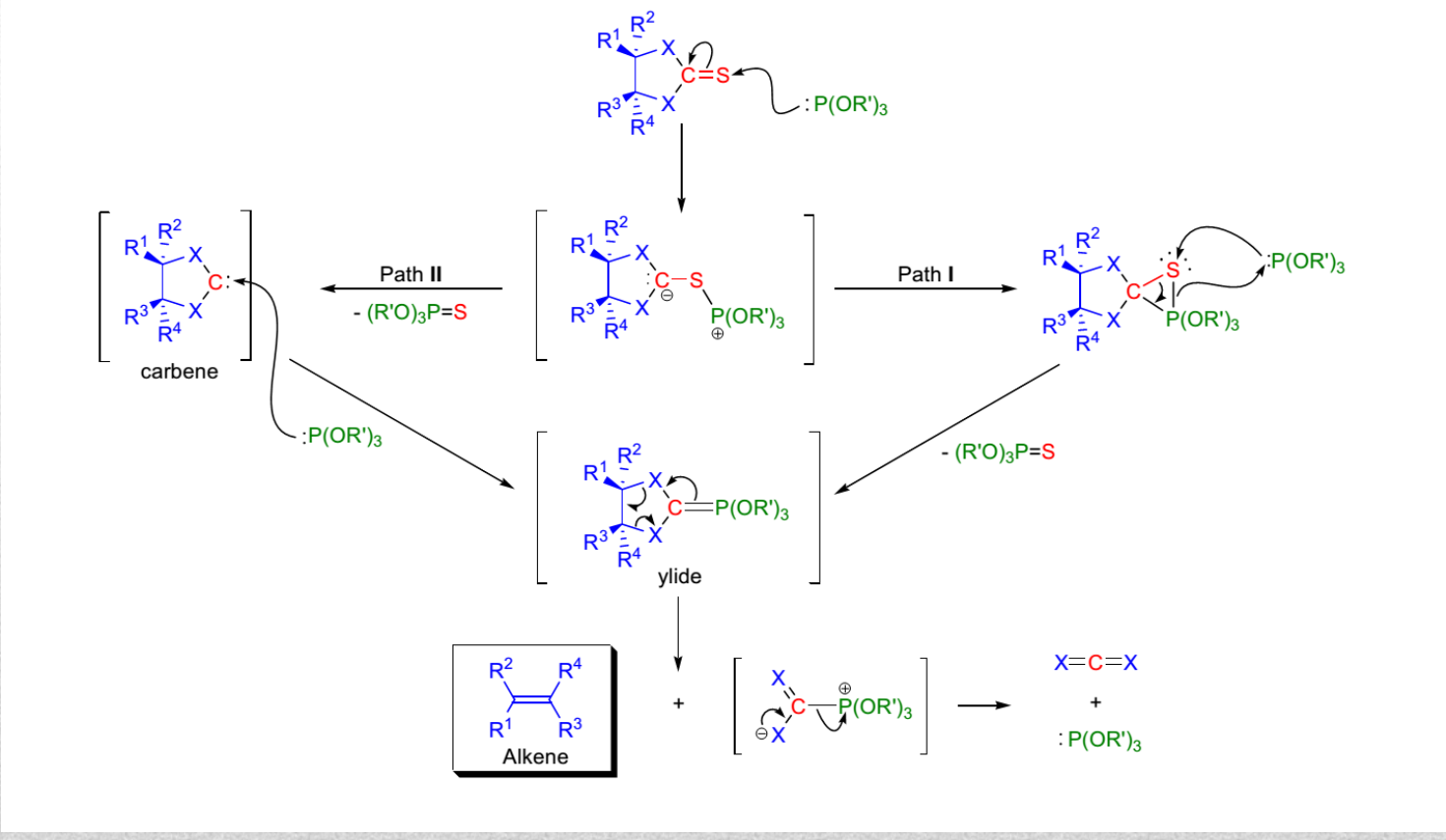
In the second step, the thionocarbonate is treated with excess trialkylphosphite [P(OR')3, where R'=Me, Et or alkyl] at reflux, and a cis-elimination reaction takes place to yield the alkene and by-products [CO2and (OR)3P=S]

Advantage

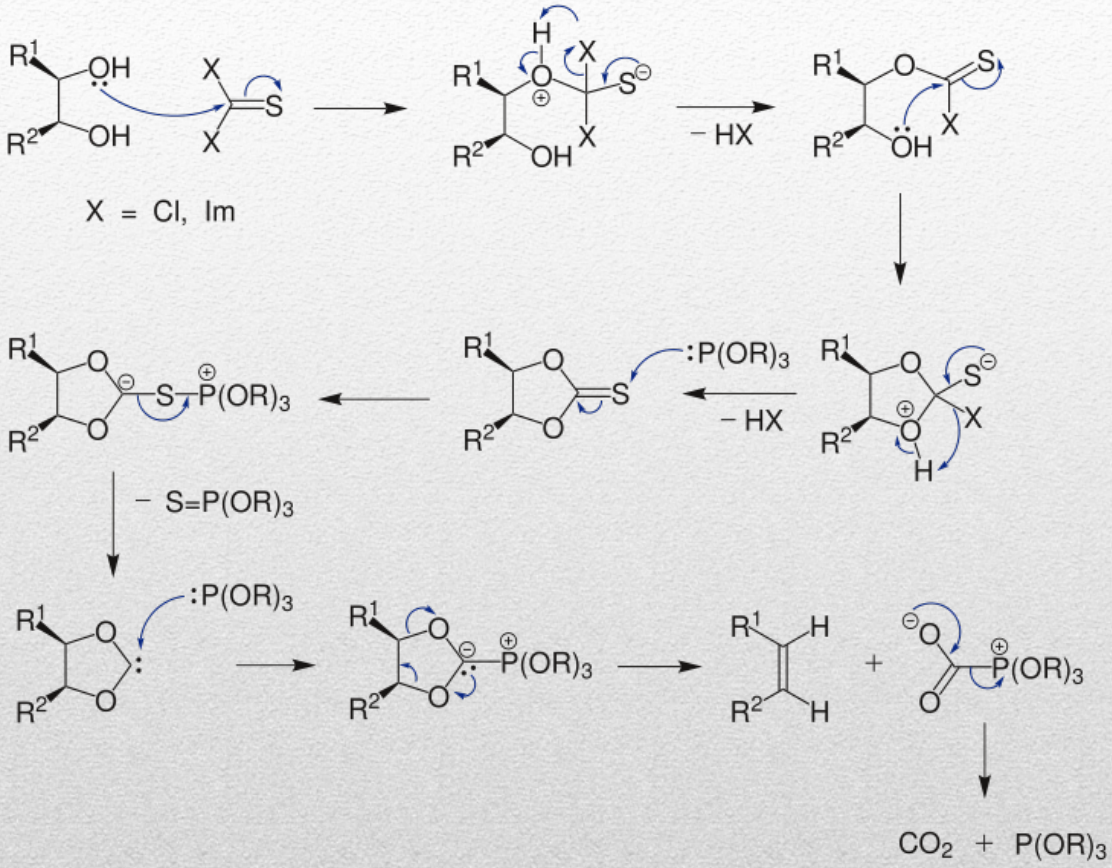
The reaction is completely **stereospecific** and **high-yielding**.

Even highly substituted and strained olefins (e.g., trans-cycloheptene) can be prepared.

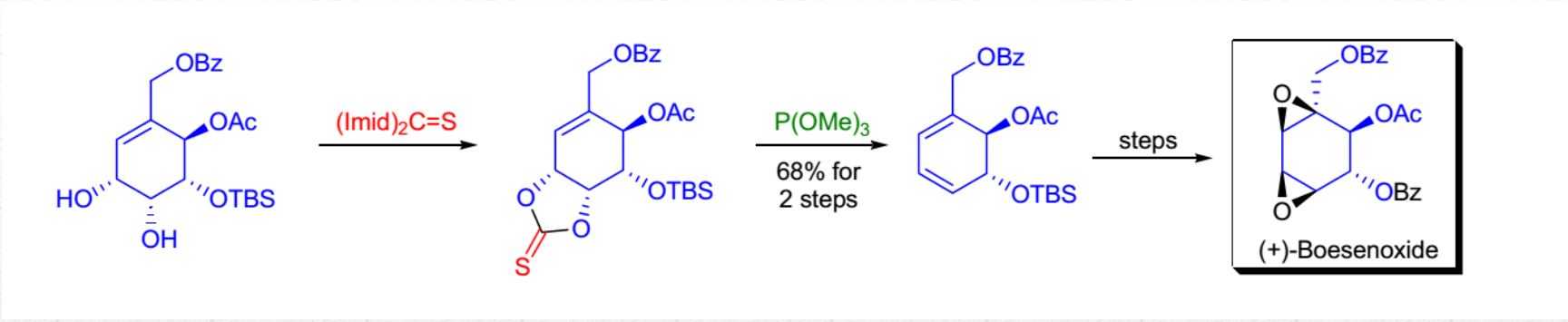


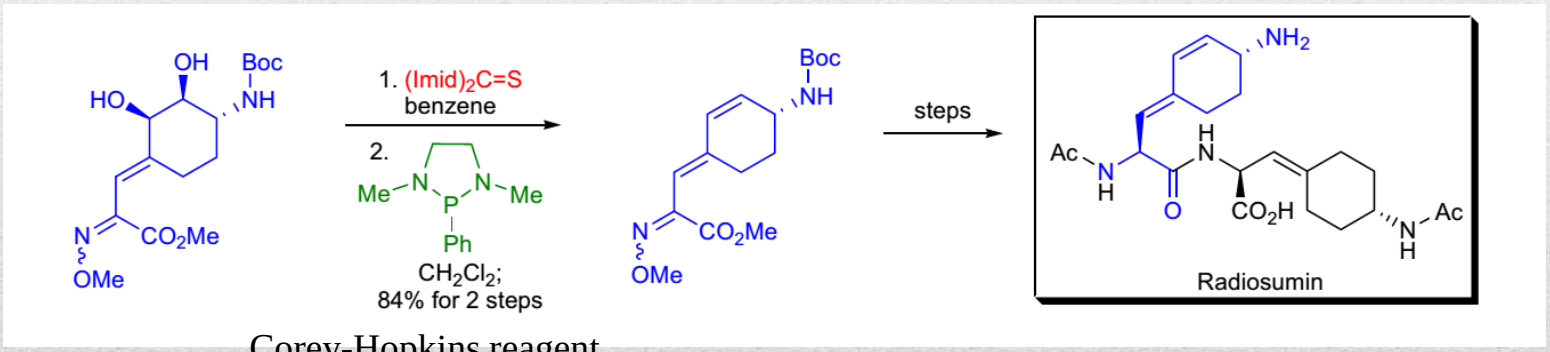

:P(OR')3
Path II
- (R'O)3P=S
Path I
:P(OR')3
carbene
:P(OR')3
- (R'O)3P=S
ylide
Alkene
+
X=C=X
+
:P(OR')3

Mechanism



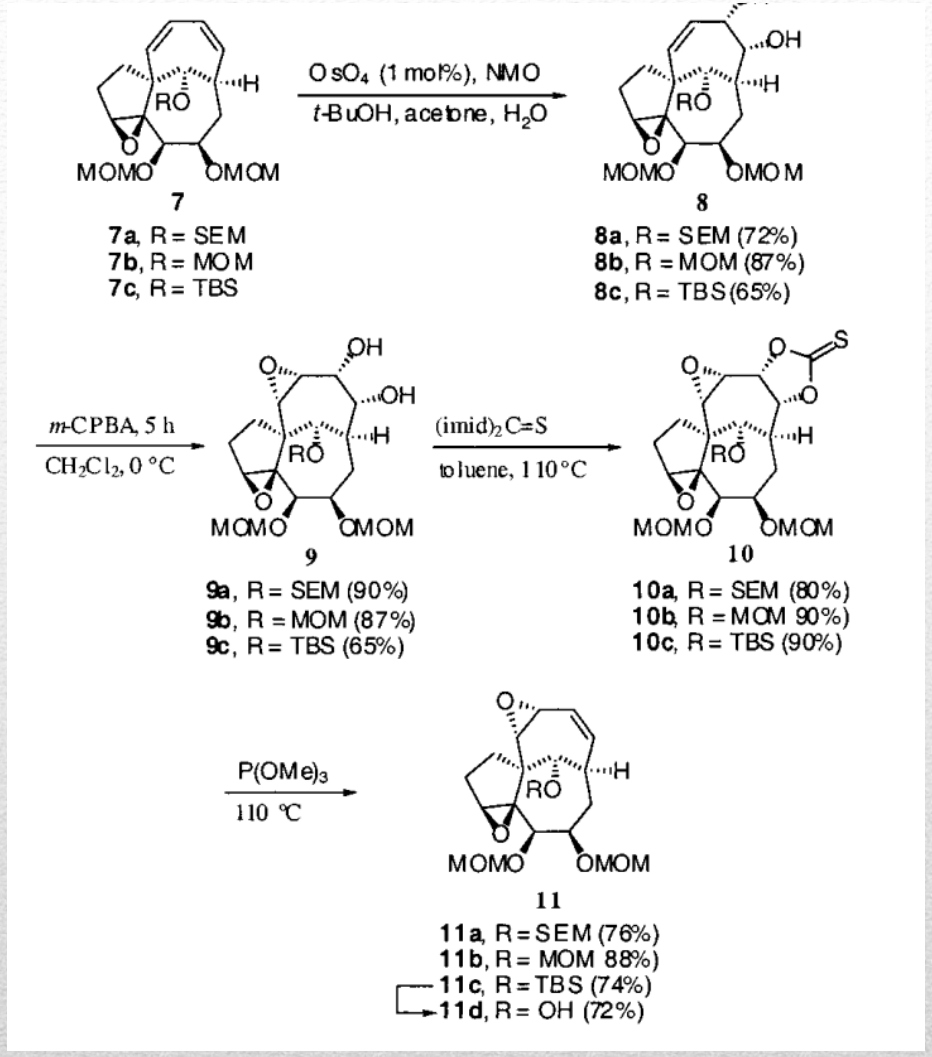
Improvement



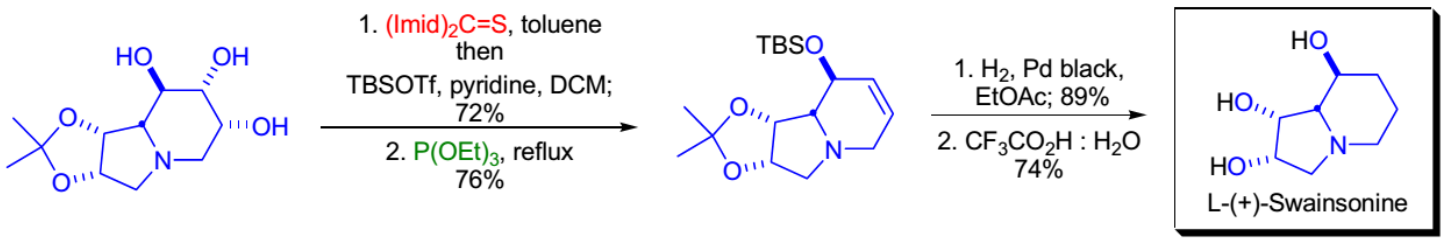


Corey-Hopkins reagent

Synthetic Applications



Synthetic Applications



Synthetic Applications

Thank you