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A NOVEL AND USEFUL SULFUR YLIDE REACTION

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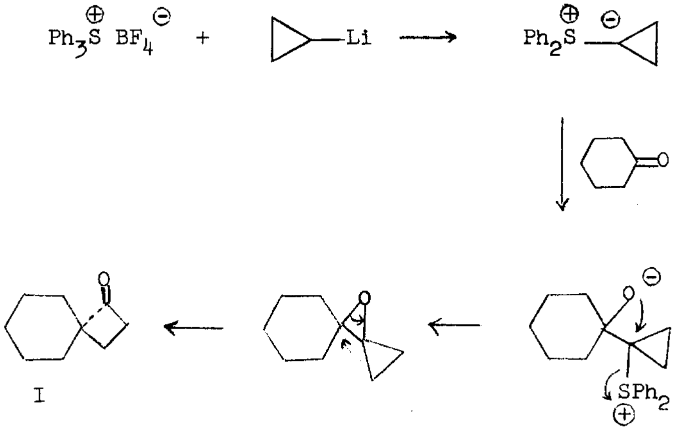
The utility of sulfur ylides in organic synthesis becomes more apparent as the volume of literature dealing with such intermediates grows. Recently, we reported a new method to generate sulfur ylides via reaction of triphenylsulfonium fluoroborate and an alkyllithium.[2] Such a method makes available ylides that would be difficult to obtain because of inaccessibility of the corresponding sulfonium salt. In this paper, we wish to report the preparation of diphenylsulfonium cyclopropylide and its novel reaction with cyclohexanone.[3]

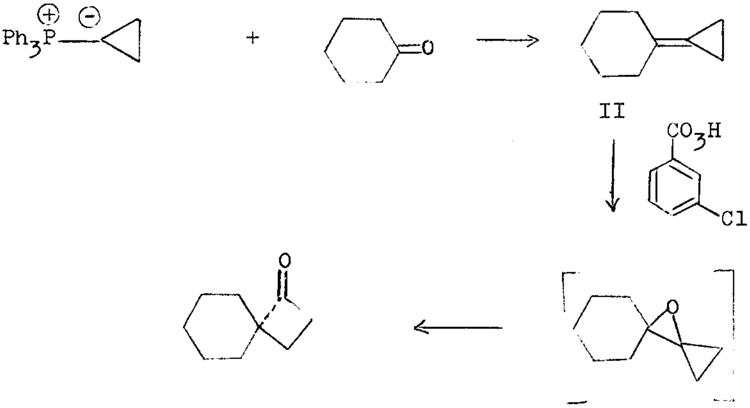
Treatment of triphenylsulfonium fluoroborate with cyclopropyllithium[4] generated a yellow slurry. After 30 minutes addition of cyclohexanone destroyed most of the color. Analysis of the reaction mixture after workup revealed the presence of a ketonic material corresponding to a molecular formula of $C_9H_{14}O$.[5] Its nmr spectrum showed a 2H triplet at 2.87 δ ($J = 8.5$ Hz) and a 12H multiplet between 1.20δ and 1.95δ. Its infrared spectrum was most informative for it exhibited a strong carbonyl absorption at 1775 cm^{-1} strongly indicative of a cyclobutanone. Its mass spectrum in addition to exhibiting a molecular ion at m/e 138 showed strong peaks corresponding to loss of ethylene (m/e 110) and ketene (m/e 96). All of this data strongly suggests the spiro cyclobutanone structure I (see Scheme I).

Scheme I. Generation and Reaction of Diphenylsulfoniumcyclopropylide



Confirmatory evidence arose through independent synthesis as outlined in Scheme II. Condensation of triphenylphosphoniumcyclopropylide[6] with cyclohexanone produced the olefin II. Peracid oxidation generated the epoxide which underwent rearrangement to the cyclobutanone I. Comparison of the two samples demonstrated identity.

Scheme II. Phosphorus Ylide Based Synthesis



Scheme I presents a rationalization for the origin of I in the sulfur ylide reaction. Normal carbonyl addition of the ylide is followed by intramolecular displacement of diphenylsulfide by oxygen. Such a displacement at cyclopropyl carbon is indeed rare. Cleavage of the highly strained dispiro epoxide, presumably an acid catalyzed process, would be expected to occur exclusively to generate an incipient cation at the cyclohexyl carbon rather than the cyclopropyl carbon. Migration of the cyclopropyl bond may occur simultaneously with or subsequently to opening of the epoxide to produce I.

Thus, this reaction provides in a single step the attachment of a spiro ring at a carbonyl carbon -- an exceedingly useful transformation for which we propose the term spiroannelation.

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