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Intramolecular Trapping of an Ylide Intermediate in the Reaction of $^1{:}CH_2$ with an Allylic Alcohol

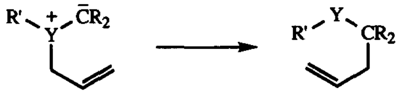
Warunee Sobery and JoAnn P. DeLuca*

Department of Chemistry, 4160 Illinois State University, Normal, IL 61790-4160

Abstract: The reaction of $^1{:}CH_2$, generated by the photolysis of CH_2N_2, with 2-methyl-3-buten-2-ol leads to the formation of several products including 4-methyl-3-penten-1-ol. This product is best explained as the result of rearrangement of an ylide intermediate.

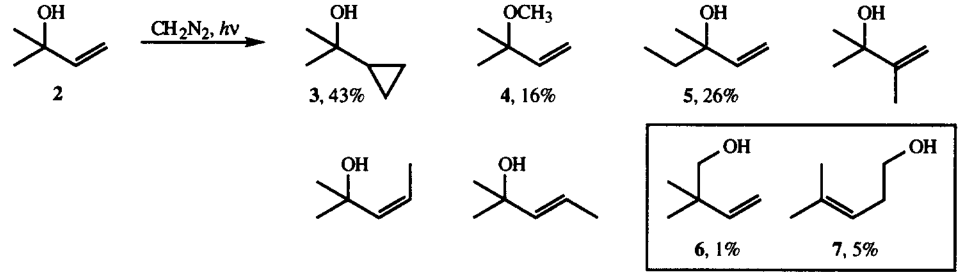
Considerable effort has gone into determining the pathways by which a variety of singlet carbenes react with alcohols to give O-H insertion products.[1] In general, electrophilic carbenes react with alcohols to form ylide intermediates which undergo either inter- or intramolecular proton transfer to yield O-H insertion products. However, the pathway for reaction of the parent carbene, $^1{:}CH_2$, with alcohols remains uncertain. Computational studies predict that the ylide formed by reaction of $^1{:}CH_2$ with water (H_2O-CH_2, **1**) will rearrange to CH_3OH with little or no enthalpic barrier,[2] supporting a concerted pathway for O-H insertion by this carbene. In contrast, Wesdemiotis et al. report a lifetime on the order of 10^{-6} s for **1** formed in neutralization-reionization mass spectrometry experiments.[3] Here we report what we believe to be the first evidence for an ylide intemediate in a reaction of $^1{:}CH_2$ with an alcohol in solution.

The involvement of ylide intermediates in reactions of singlet carbenes with allylic substrates has often been inferred from the formation of rearrangement products.[4] Rearrangement of allylic ylides as shown in eq 1 may occur as either a concerted 2,3-sigmatropic shift or via homolytic cleavage of the heteroatom-carbon bond to form a radical pair (Stevens rearrangement).[5] In cases where the ylide can be readily prepared, yields of rearrangement products are often high enough to make the rearrangement synthetically useful.[4c] Moss et al. have used laser flash photolysis to study sulfonium ylides resulting from attack of chlorophenylcarbene on allylic sulfides and found their rearrangement to be quite rapid ($k \approx 10^7\ s^{-1}$ at room temperature).[6] These features suggested to us that a rearrangment of this type might be very well-suited to the trapping of an ylide formed as a short-lived intermediate in the reaction of $^1{:}CH_2$ with an allylic alcohol.



(1)

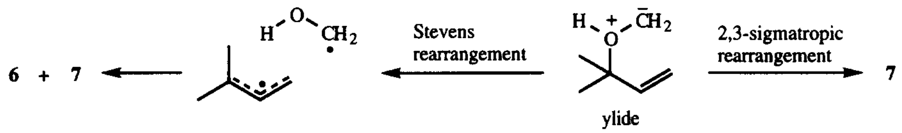
We carried out the reaction of $^1{:}CH_2$, generated by photolysis of CH_2N_2, with 2-methyl-3-buten-2-ol (**2**) in pentane solution (eq 2).[7] Products arising from reaction of the carbene with substrate **2** were identified by comparison (GC coinjection and GC/MS) with, and GC response factors were measured for, authentic samples. The products of carbene addition to the double bond (**3**), insertion into the O-H bond (**4**) and insertion into the methyl C-H bonds (**5**) were identified in the reaction mixture. Three additional products, formed in lesser



(2)

amounts, were not thoroughly characterized, but were assumed to be vinylic C-H insertion products. Alcohols **6** and **7** were also identified. The product distribution is indicated in eq 2.

The products and their distribution are unremarkable, except for the appearance of compounds **6** and **7**. Formation of **6** may proceed from an ylide intermediate via the Stevens rearrangement as shown in eq 3, although a direct C-O insertion of the carbene cannot be ruled out rigorously. Formation of **7** must involve a rearrangement, most reasonably 2,3-sigmatropic rearrangement, or possibly Stevens rearrangement, of an oxonium ylide intermediate. Thus, our results indicate that an ylide intermediate is formed in the solution phase reaction of ^{1}:CH_2 with alcohol **2** and that rearrangement of the ylide to alcohol **7** can successfully compete with both inter- and intramolecular proton transfer.



(3)

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