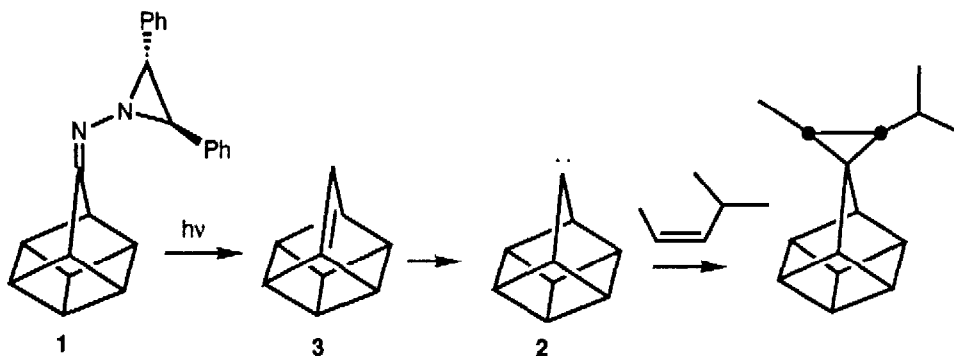


AN EQUILIBRATING CARBENE-BRIDGEHEAD ALKENE PAIR¹

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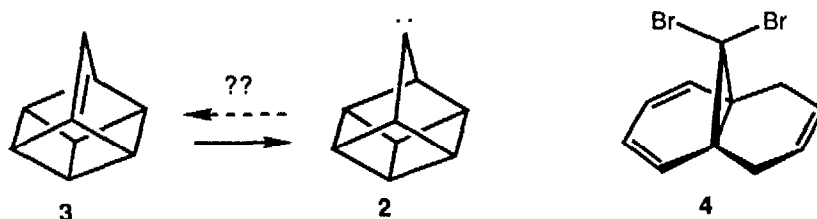
Abstract: Development of a new source of alkylcarbenes allows the direct formation of homocuban-9-ylidene. Deuteriomethanol traps not only the carbene, but the product of its rearrangement, the bridgehead alkene homocub-1(9)-ene. Together with the earlier observation that the bridgehead alkene rearranged to the carbene this demonstrates the first example of an equilibrating carbene-bridgehead alkene pair.

DECOMPOSITION of **1**, a potential precursor of homocuban-9-ylidene (**2**) in alkenes leads to cyclopropanes. The apparent simplicity of this reaction is an illusion, as the first formed intermediate from **1** has been shown to be the bridgehead alkene **3**, homocub-1(9)-ene, which rearranges to **2**.²

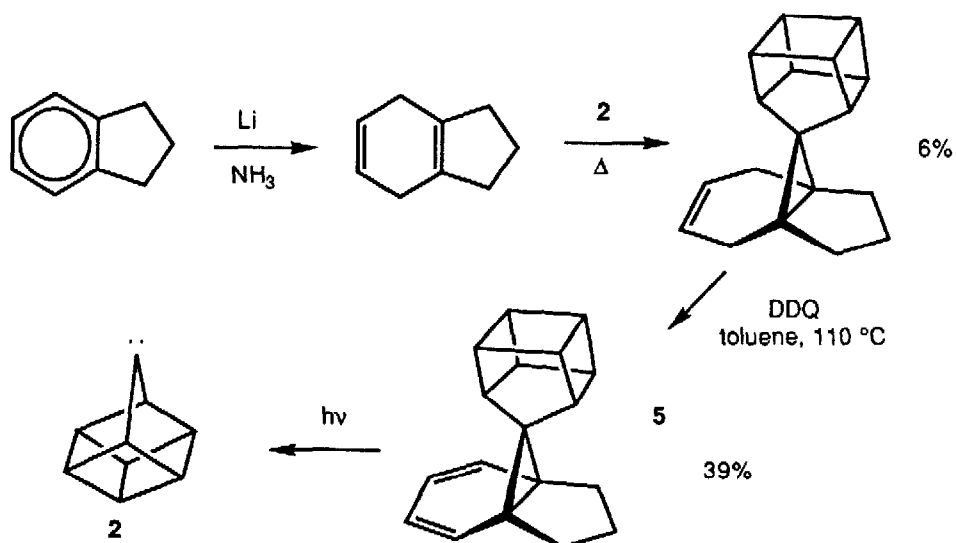


Intramolecular reactions of precursors are likely to be important in photochemical decompositions of simple diazo compounds and diazirines³ and there is evidence that even in thermal reactions some of the products derive not from the carbene but from direct rearrangement of the starting material.⁴ Therefore it is not surprising to find direct rearrangement in the homocubyl (and probably cubyl) systems which are notoriously prone to ring expansions.⁵

In this Letter we address the question of whether the alkene-to-carbene rearrangement (**3** \rightarrow **2**) is reversible. Can the carbene form the bridgehead alkene? If it does, **2** and **3** become the first known equilibrating carbene/bridgehead alkene pair.

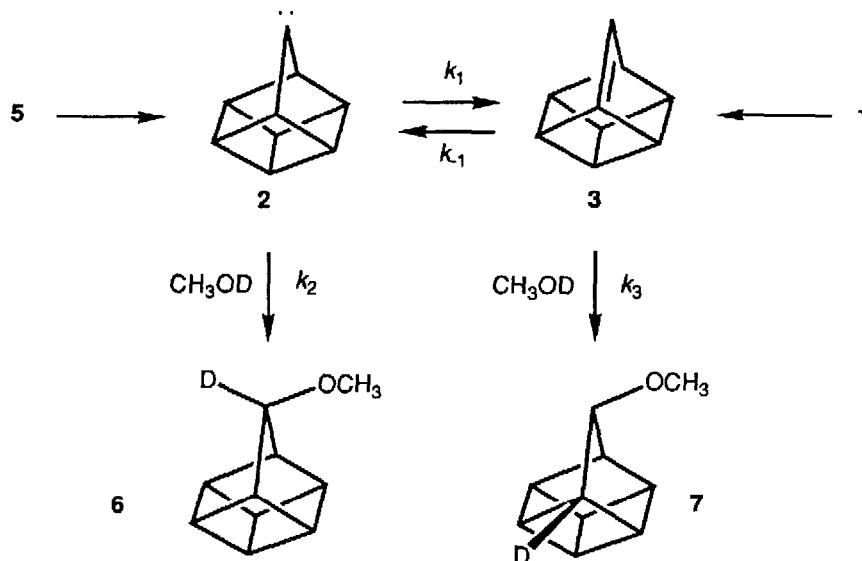


Probably the most simple way to attack this question is to find a way of generating the carbene **2** without the possibility of direct formation of **3** and to probe for the formation of **3** through trapping experiments. It was known from our earlier work that deuteriomethanol was able to trap both **2** and **3**,² so the most difficult task was to find a non-diazo source of the carbene. We had shown that dihalocarbenes could be efficiently generated photochemically from **4**,⁶ and the following sequence leading to **5** seemed a promising extension:



Although only a masochist would use this sequence to make large amounts of **5** (the addition reaction of **2** to dihydroindan gives >80% of the "wrong" adduct) it does suffice to make the hundred milligrams necessary for this mechanistic study.

Irradiation of **5** in deuteriomethanol gives *both* **6** and **7**, and we can immediately see that **2** and **3** are in equilibrium.

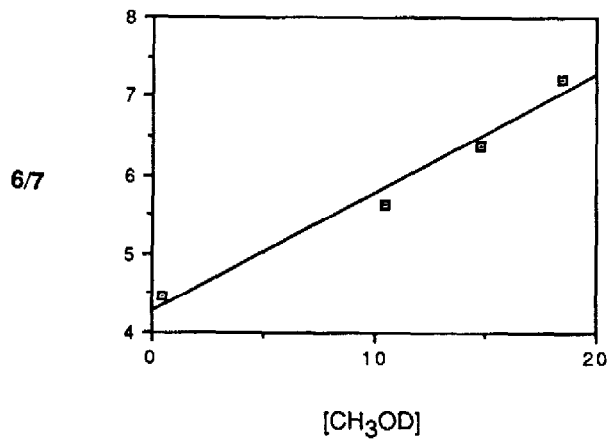


A plot of **6/7** vs. $[\text{CH}_3\text{OD}]$ is linear with a positive slope (equation 1).

$$(\mathbf{6/7} = 4.27 + 0.15[\text{CH}_3\text{OD}], R = 0.99)$$

Equation 1

This reinforces the notion that the carbene must be the first formed intermediate from **5**, as it is the product of its trapping that increases with $[\text{CH}_3\text{OD}]$.



Moreover, one can use equation 1 along with equation 2, which links the ratio 6/7 to [CH₃OD] under pseudo first order conditions, to generate further information, although the value of the equilibrium constant relating 2 and 3 remains unknown.

$$6/7 = k_2 k_{-1} / k_1 k_3 + k_2 / k_1 [\text{CH}_3\text{OD}] \quad \text{Equation 2}$$

Thus $k_1/k_2 = 6.67 \text{ M}$, and $k_{-1}/k_3 = 28.5 \text{ M}$. The equilibration of 2 and 3 is faster than either of the trapping reactions with deuteriomethanol, but not enough so that the ratio 6/7 becomes independent of the entry point to the equilibrium.

References and Notes:

1. Support for this work by the National Science Foundation through Grant 8800448 is acknowledged with thanks. We also thank Dr. K. G. Valentine for expert assistance with the ²H NMR measurements.
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