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A Zipper Mechanism for the Carboranylcarbene Rearrangement[1]

Rodney J. Blanch, Kaixu Yuan, and Maitland Jones, Jr.*

Department of Chemistry
Princeton University
Princeton, New Jersey 08544

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The phenylcarbene rearrangement was described in this journal and elsewhere over 20 years ago.[2] The mechanism of this remarkable reaction was worked out over the ensuing years, and "obvious" mechanisms in which the carbene atom walked around the outside of the ring were shown to be wrong. The reaction is now known to involve a deeper process in which ring carbons exchange places with the initially divalent carbon (Scheme I). Ring-expanded species, probably cycloheptatetraenes, are intermediates.[3]

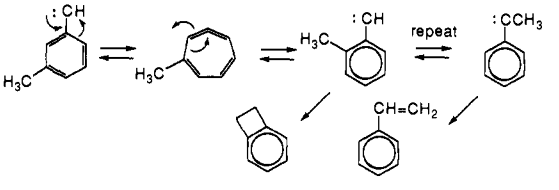
About 15 years ago we reported the carborane counterpart of this reaction, the carboranylcarbene rearrangement.[4] We showed that one of the products formed from 1-(2-methyl-*o*-carboranyl)-carbene (**1**) in the gas phase was 1-vinyl-*o*-carborane (**2**) (Scheme II). Here, we describe labeling experiments that establish the fates of the cage and carbene carbons in this rearrangement. The results eliminate simple processes taking place on the exterior of the carborane and implicate cage-expanded structures as transition states or intermediates.

Both the precedent of the phenylcarbene rearrangement and new calculations by McKee[5] suggested that the carboranylcarbene rearrangement might involve cage-expanded species. We wanted to differentiate mechanisms in which the exo-cage carbons remain outside from those in which the carbene carbon becomes incorporated into the cage. A typical unexceptional mechanism would be carbon–carbon insertion by carbene **1** to give **6**, followed by opening to the vinyl compound **2** (Scheme III). Intramolecular carbon–carbon insertions by carbenes are common,[6] and benzocyclopropene is known to rearrange by breaking one of the cyclopropane single bonds.[7]

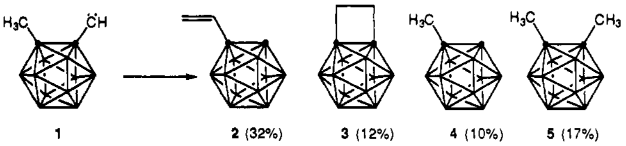
Alternately, the cage might expand to a 13-vertex framework (**7**) in which two monosubstituted carbons flank a bare central carbon (Scheme IV). The stable *o*-carborane cage can be reconstituted from such a species in two ways. In one, the lurking methyl group traps the carbene to give **2**. In such a reaction, the carbons follow each other in lockstep, as the four-carbon sequence "zippers" through the boron framework.

The single labeling experiment of 1979,[4] in which the methyl group was shown to become the terminal carbon of the vinyl group, though necessary to eliminate compound **3** as a source of **2**, is otherwise uninformative. Therefore, we synthesized diazo compounds **8** and **9** by two converging routes (Scheme V). Ester **10**, labeled in the carbonyl carbon, was made from 1-methyl-*o*-carborane by carboxylation[8] and esterification. Ester **11**, labeled in one cage position, was constructed from the reaction of decaborane with labeled methyl 2-butynoate.[9] The labeled acetylenic ester was made from acetoacetic ester through reaction with hydrazine[10] and oxidation with $Tl(NO_3)_3$.[11] The esters were converted into the corresponding aldehydes through reduction with $LiAlH_4$ and oxidation with NCS. The aldehydes were transformed into the diazo compounds **8** and **9** by the standard published procedures.[4]

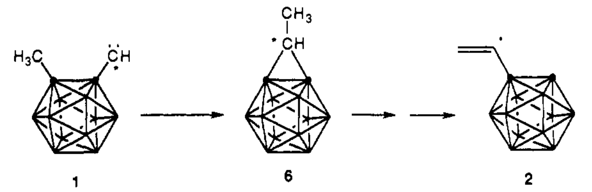
Scheme I



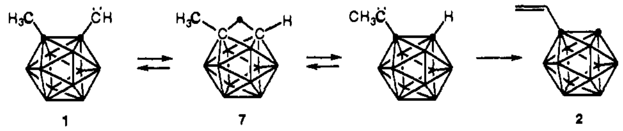
Scheme II



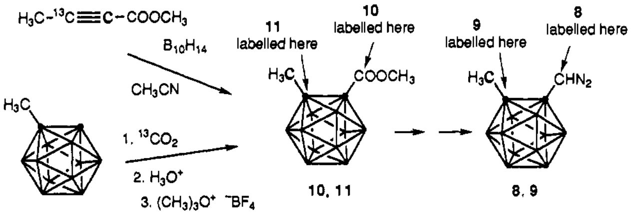
Scheme III



Scheme IV



Scheme V



The diazo compounds were decomposed at 500 °C/$<10^{-3}$ Torr by sublimation at 0 °C into the hot oven. The products were collected on a liquid nitrogen-cooled cold finger and analyzed immediately by GC/MS and ^1H and ^{13}C NMR spectroscopy of both the crude reaction mixture and pure compounds isolated by preparative gas chromatography. Under our reaction conditions, approximately 60% of **2** was converted into its meta isomer, 1-vinyl-*m*-carborane.

Examination of the ^1H and ^{13}C NMR spectra of the vinyl compounds **2** showed that, within our limits of detection of about 5%, all of the label in **8** appeared in the cage C–H, and all of the label in **9** in the vinyl C–H (Scheme VI). No other positions

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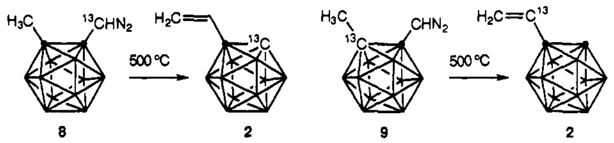
Scheme VI



appeared labeled. These results are clearly incompatible with any mechanism in which the noncage carbons remain outside the cage or with any intermediate of the symmetry of **6**. On the other hand, they are exactly what is to be expected of **7**.

Most of the other products are uninformative. The 1-vinyl-*m*-carboranes are probably formed from the ortho compounds and carry no important information. The label appears, as it should, in the unsubstituted cage carbon. Similarly, products **3** and **5** can scarcely be labeled other than in the four-membered ring and one of the methyl groups, respectively, and they are. However, the monomethyl compound **4** is potentially more interesting. Although there are many prosaic explanations for its formation,[12] were **7** to be an intermediate, it might lose a carbon atom to give **4**. This would produce labeled **4** from **8**. However, this seems not to be the case, as we find no label in the cage C–H of **4**. Small amounts (~5%) would escape our detection, but there can be no wholesale incorporation of label into **4**.

McKee's calculations[5] hint that species such as **7** may be energy minima. Although our work implicates **7** in this reaction, we cannot speak to the question of whether **7** is an intermediate or a transition state for the conversion of **1** into **2**. Nevertheless, **7** is now a permissable intermediate in the carboranylcarbene rearrangement, and a cage expansion of some kind seems required.

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[12] Reaction with a wall followed by bond-breaking and azine formation followed by loss of HCN are two possibilities.