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A NOVEL REACTION OF *VIC*-DIORGANOBORANES[1]

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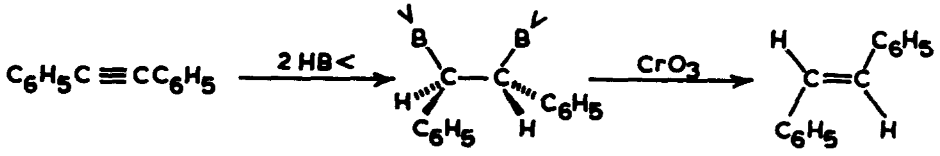
A recent publication[2] from our laboratory proposed a mechanistic scheme for the formation of the major product, cyclotridecene formed by dihydroboration of 1,2-cyclotridecadiene followed by reaction with CrO_3. We proposed that the possible *vic*-diorganoborane intermediate probably undergoes an elimination reaction to give the cyclotridecene. The substantiation or refutation of the proposed reaction pathway awaited the preparation of an authentic *vic*-diorganoborane and study of its reaction with CrO_3.

We have now prepared *threo*-*vic*-diorganoborane (2) from diphenylacetylene (1) by dihydroboration as described by Pasto[3]. Although the reason for preferential formation of 2 over *gem*-diorganoborane is not clear, Pasto[3] suggested that it may be partly due to the complex polymeric nature of the intermediate, *cis*-vinyl organoborane. The treatment of 2 with CrO_3 in pyridine produced *trans*-stilbene (3) as the only isolated product in 70% yield (Scheme 1). The identity of 3 was established by mixed mp and comparison of the ir spectrum

Scheme 1

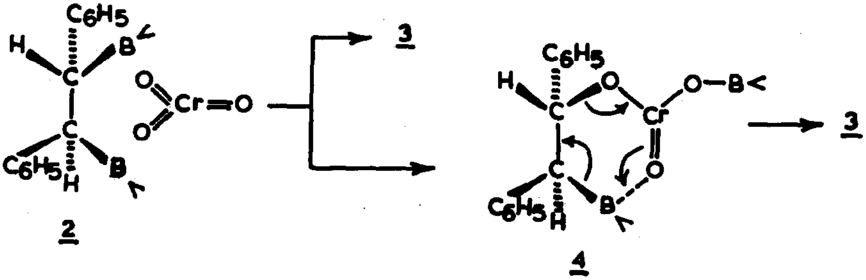


1   2   3

with that of an authentic sample. Thus, our results demonstrate that the deboronation of 2 occurs exclusively by *cis*-elimination.

We suggest that the probable mechanism of this new elimination reaction could involve either a one-step or two-step process (Scheme 2). In the concerted process, a seven-membered transition state having 8 electrons is invoked. Alternatively, the first step of a two-step process could involve the breakage of the Cr-O d-p π-bond to form a B-O bond, and the take-up of the d-p π-electrons by the chromium atom which results in 4. The stereochemistry of the reaction can be explained as the electron-deficient boron is capable of complexing with oxygen of the CrO_3 in 4. The intermediate 4 can undergo cleavage of the bonds as shown in the Scheme 2 to produce 3.

Scheme 2



In conclusion, the present study confirms the previous suggestion that *vic*-diorganoboranes can undergo unusual elimination reactions with CrO_3 to form alkenes instead of 1,2-diketones, the expected oxidation products. Currently we are studying the reactions of *gem*-diorganoboranes with CrO_3, and our results will be discussed in a later publication.

References

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2. I. Mehrotra and D.Devaprabhakara, Tetrahedron Letters, 4871 (1972).
3. D.J.Pasto, J.Amer.Chem.Soc., 86, 3039 (1964).