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REACTIONS OF 1,2-DIORGANOBORANES WITH ALKALINE SILVER NITRATE - A NEW ROUTE TO OLEFINS

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The organoboranes as synthetic intermediates have created immense interest since the discovery of the reaction of diborane with alkenes and related unsaturated compounds.[1,2] Brown and coworkers[3] have shown that the reaction of trialkylboranes with alkaline silver nitrate provides a convenient synthesis of symmetrical and unsymmetrical hydrocarbons. Very recently this reaction has been extended to cyclize a variety of dienes.[4] The following communication will illustrate the application of such a free-radical coupling reaction to the synthesis of olefins from some representative internal acetylenes.

We wish to report that dihydroboration of internal acetylenes such as 5-decyne, 2-nonyne, diphenylacetylene and cyclotridecyne followed by excess alkaline silver nitrate treatment proceeds to give the corresponding olefins in good yields. The results are summarized in the TABLE. In the case of acyclic dialkyl substituted acetylenes we have observed almost an exclusive formation of E-olefins which exhibit purity in the neighbourhood of 98%. In the case of diphenyl substituted and large-ring acetylene, the reaction results in the predominant formation of E-olefins.

The threo-1,2-diorganoboranes were prepared from acetylenes as described by Pasto.[5] The procedure used for the reaction of 1,2-diorganoboranes with alkaline silver nitrate follows essentially that of Murphy and Prager[4] except for the time of reaction (2 hr at room temperature).

TABLE

Products of Reaction of Some Internal Acetylenes with BH_3-THF Followed by Alkaline Silver Nitrate:

Acetylene[a]	Olefinic Product(s)[b]	Yield[c]
5-Decyne	trans-5-Decene	72%
2-Nonyne	trans-2-Nonene	75%
Diphenylacetylene	trans-Stilbene (90%) cis-Stilbene (10%)	89%
Cyclotridecyne	trans-Cyclotridecene (78%) cis-Cyclotridecene (22%)	75%

a Acetylenes were prepared by known procedures and thoroughly characterised prior to use.

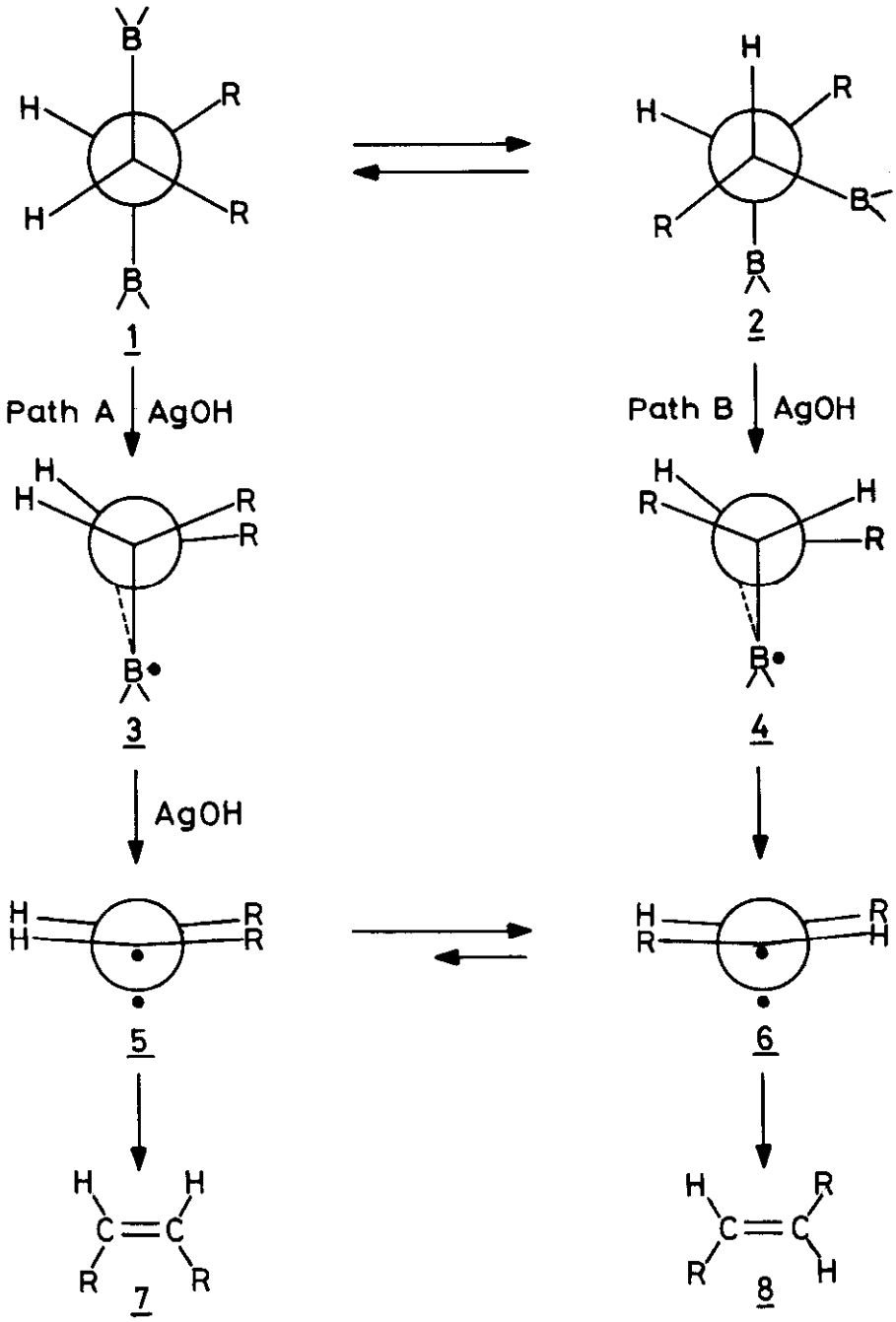
b The identify of the individual product(s) was established by comparison of GLC retention times (Carbowax 20M) and IR spectra with those of the authentic samples.

c Isolated yield.

The plausible pathways for the formation of olefins from threo-1,2-diorganoboranes are shown in the SCHEME. The stable conformations for the threo-1,2-diorganoboranes are represented by conformer 1 and 2 which could exist in equilibrium. We visualize the formation of E-olefin (8) via path A and B. The reaction between trialkylborane and alkaline silver nitrate has been suggested to give free-radical species via organosilver compound.[6] Therefore, in path A, the Z-1,2-diradical species (5), generated via Z-bororadical species (3) could change over to more stable E-diradical species (6) by bond rotation before it collapses to 8. In path B, the E-diradical species (5) formed via E-bororadical species (4) can also yield 8. The preferential pathway adopted by the threo-diorganoborane may depend upon (a) the bulkiness of the R groups, (b) the bulkiness of the substituted borons, (c) the stability of the diradical species, (d) the size of the ring and (e) the energy barrier for Z,E isomerization. We favour the path B involving no equilibration of diradical species (5 and 6) for the stereoselective reduction of acyclic dialkyl substituted acetylenes. The formation of the minor product,

SCHEME

Possible mechanistic pathways for product formation



Z-olefin in the case of cyclotridecyne may be visualized mainly via path A. In the case of diphenylacetylene we feel that the equilibrium between 5 and 6 might become important. However, the formation of olefins from the small amount of 1,1-diorganoborane (~5%) formed during dihydroboration of acetylenes cannot be ruled out.

Thus, the present procedure provides a useful method for the conversion of acyclic dialkyl substituted acetylenes to E-olefins of high stereochemical purity. Currently work is in progress with bulky dialkyl substituted and medium-ring acetylenes. We also plan to carry out similar reactions with 1,1-diorganoboranes.

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