

Di- π -methane-like photorearrangements of α,β -unsaturated organoboranes in the synthesis of borirenes and boracarbenoid intermediates

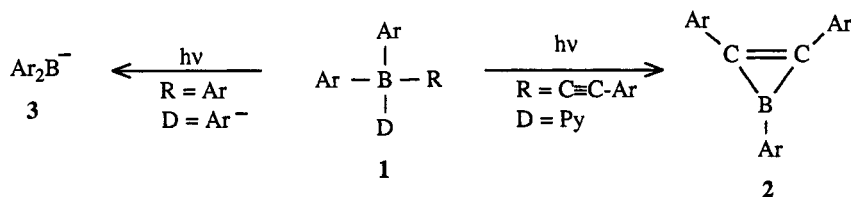
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Abstract - The photoisomerization of α,β -unsaturated organoboranes, either as the neutral coordination complex with tertiary amines ($R_3B \cdot NR_3'$) or as the anionic complex with organoalkali compounds (R_4B^-), leads, via a 1,2-shift of organic groups from boron to the adjacent carbon, to three-membered boracarbocycles or to the eventual α -elimination of R_2 and the generation of subvalent organoboranes reminiscent of boron analogues of carbenes. These alternative reaction pathways will be illustrated by the photogeneration of the boracyclopropene ring and by the production of RB and R_2B^- boracarbenoids.

INTRODUCTION

In recent studies we have found that α,β -unsaturated organoboranes (**1**), either as the neutral coordination complex or as the complex with organoalkali compounds, undergo interesting 1,2-photorearrangements of organic groups bonded to boron with the shift of such organic groups to adjacent unsaturated carbon (ref. 1 and 2, note a):

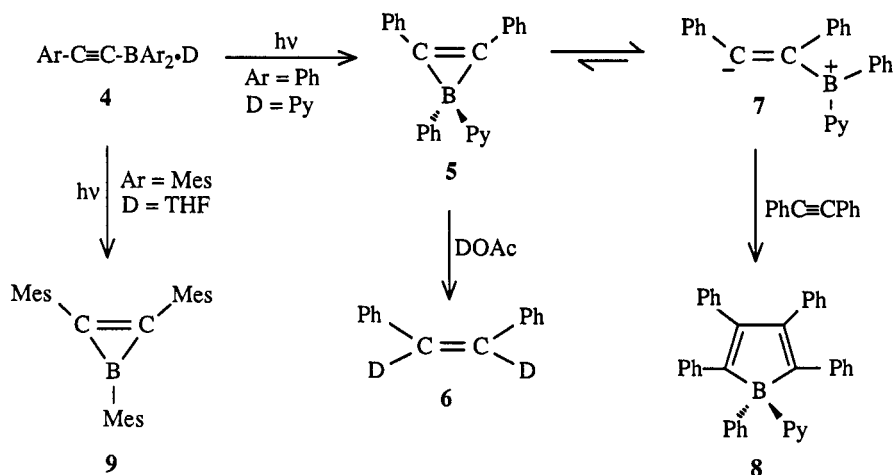


Such 1,2-photoshifts are reminiscent of di- π rearrangements of unsaturated carbon systems, as extensively investigated by Zimmerman and co-workers (ref. 3). Depending upon the nature of the substituents in the organoborane complex, such 1,2-photoshifts can produce the interesting unsaturated boracarbocycle, the borirene nucleus (**2**), or these rearrangements can lead to the elimination of biaryls and the generation of the diarylborate(I) anion (**3**), which is isoelectronic with a carbene. This lecture will explore the conditions under which the borirene (boracyclopropene) nucleus is generated and those conditions where the boracarbenoid anion is formed. Crystal X-ray data will be adduced to demonstrate that diaryl(arylethynyl)boranes photoisomerize to triarylborirenes (**2**), while the results of chemical trapping experiments with ethers, alkynes and organic halides will be presented to support the photogeneration of ArB from $Ar_3B \cdot Py$ and of Ar_2B^- from Ar_4B^- . Finally, evidence will be assessed as to whether such boracarbenoids can also be generated from the metal-induced dehalogenation of haloorganoboranes.

Note a: Part 13 of Bora-Aromatic Systems. Previous part: J.J. Eisch, J.E. Galle, B. Shafii and A.L. Rheingold, *Organometallics*, **9**, 0000 (1990). The authors gratefully acknowledge the support of the National Science Foundation through Grant CHE-87-114911.

BORIRENES

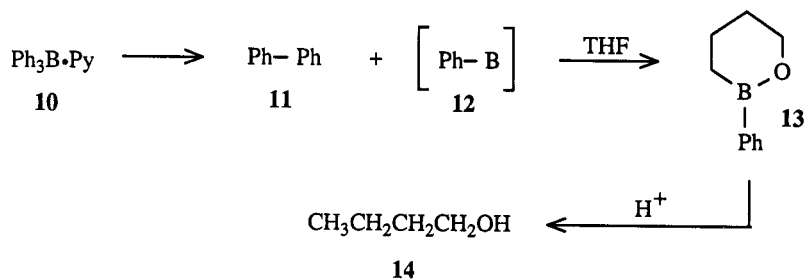
Some 15 years ago, we observed that the irradiation of the diphenyl(phenylethynyl)borane-pyridine complex (4) at 254 nm gave an intermediate that upon treatment with DOAc provided α, α' -dideuterio-*cis*-stilbene (6) in > 90% yield. Although the detection of 6 was consistent with the presence of precursor borirene 5 the borirene could not be isolated as such, even though its open-chain isomer 7 could be trapped in high yield as its cycloadduct with diphenylacetylene, the pentaphenylborole-pyridine adduct (8) (ref. 4):



Subsequent research has shown that the presence of strong donors, such as pyridine, favors the ring-opening of 5 and the formation of 7. By using sterically demanding substituents in 4 (Ar = mesityl or 2,6-dimethylphenyl) and weaker donors (THF), the photogenerated borirenes, such as 9, can be isolated and their ring-cleavage reactions with pyridines, alcohols, acids and dioxygen studied in detail. Furthermore, a suitable single crystal of 2-(2,6-dimethylphenyl)-1,3-dimesitylborirene revealed the ring atom separations of the boracyclopene array as C=C, 1.380; C₁-B, 1.450; and C₂-B, 1.464 Å. These bond distances are consistent with the occurrence of π -electron delocalization and thus aromaticity in the borirene nucleus (ref. 5).

BORACARBENOID INTERMEDIATES BY PHOTOLYSIS

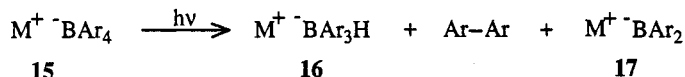
The irradiation of the triphenylborane-pyridine complex (10) in THF solution at 254 nm reveals, upon acetolysis, the presence of biphenyl (11), terphenyl and *n*-butyl alcohol (14). The biphenyl (and ultimately the terphenyl) can be ascribed to a 1,2-aryl shift from boron to carbon, with subsequent generation of a phenylboron(I) intermediate (12); insertion of 12 into the THF could then produce 13 and, upon hydrolysis, 14 (ref. 6 and 7):



Such photolysis solutions of 10 exhibit strongly enhanced reducing properties.

In an analogous fashion, the irradiation of alkali metal tetraarylborates

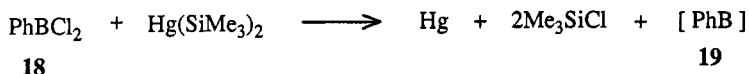
(15) in tetrahydrofuran or in 1,2-dimethoxyethane yields, upon hydrolysis, biphenyl, *m*- and *p*-terphenyls and dihydrogen. Again, such photolysates exhibit strongly reducing properties, which stem from the photogenerated borohydrides (16) and subvalent boron intermediates present. An array of converging results from chemical trapping experiments (with DOAc, $R-C\equiv C-H$, $R-C\equiv C-R$ and $PhCH_2Cl$) indicate that a diarylborate(I) anion (17) is generated photochemically (ref. 2, 8 and 9):



Whether 17 persists as such in the photolysate, undergoes association to an oligomeric anion (e.g., $[B_2Ar_4]^{2-}$) or disproportionates to other boron cluster ions (e.g., $[BAr_3]^{-}$ and $[BAr]^{n-}$) is unknown at present (ref. 11).

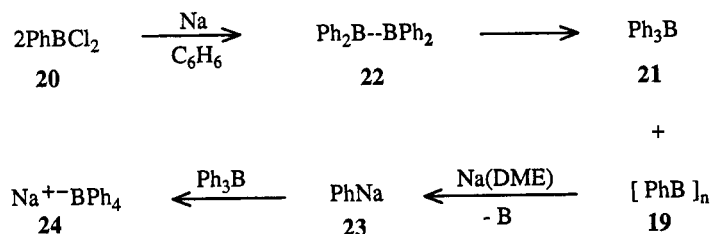
BORACARBENOID INTERMEDIATES BY REDUCTION

Attempts to generate subvalent arylboranes or arylborates(I) anions by the reduction of arylboron halides have uncovered some thought-provoking observations. Treatment of phenylboron dichloride (18) with bis(trimethylsilyl)mercury in a 1:1 molar ratio yields some phenylboron(I) oligomer (19), from which Ph_3B can then be isolated by disproportionation (ref. 10):



Similar reductions of diphenylboron chloride (20) by sodium metal can be followed in a stepwise fashion by commencing the reaction in benzene. With ultrasonic promotion an initially formed yellow precipitate can be generated with only unchanged 20 detectable in solution by ^{13}C NMR spectroscopy. Addition of stoichiometric amounts of DME (3 times the amount of Na) yields a yellow solution in which 20, Ph_3B (21) and an unknown borane (22) are clearly evident. Signals due to 22 sharply diminish with further reaction time. When 20 is allowed to react with 2 equivalents of sodium in DME alone, triphenylborane is the first observed product in solution. At longer times the signals of sodium tetraphenylborate (24) finally appear. For both reactions in benzene and in DME some insoluble material remains: this material is a mixture of NaCl and boron-containing products. These observations suggest the following sequence of reactions:

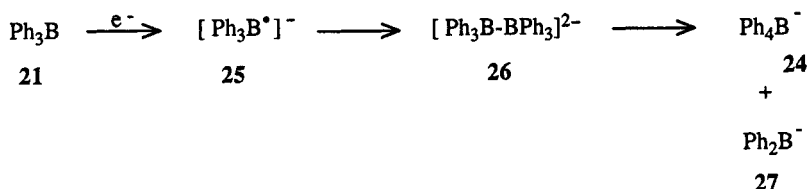
Scheme I



The unknown borane 22 formed in benzene is most likely tetraphenyldi-borane(4), which in DME with Na may rapidly disproportionate into 21 and the previously described polymeric 19 (ref. 12 and 13). Reaction of 19 with Na in DME would be expected to generate phenylsodium (23) in a metalloid-sodium displacement reaction.

Electrochemical studies of the reduction of triphenylborane (**21**) support the occurrence of a reversible formation of the radical-anion (**25**), an irreversible generation of the dianion (**26**) and the disproportionation of the latter (Scheme II, ref. 14):

Scheme II



These observations open up an alternative pathway for the conversion of Ph_2BCl into NaBPh_4 than that depicted in Scheme I: Ph_3B could be the simultaneous source of NaBPh_4 and NaBPh_2 (**27**) via its 1 : 1 and 1 : 2 adducts (**27**) and **27**. Admittedly, the presence of **27** (said to absorb at 333 nm) in the sodium metal reduction of Ph_2BCl has not yet been established. Nevertheless, the electrochemical results do hold out the hope that the diphenylborate (I) anion, which is suggested to arise from **24** photochemically, may also be generated from Ph_2BCl by alkali metal-reduction (ref. 11).

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