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GENERATION AND CAPTURE OF TRIPHENYLBORIRENE IN THE DI-π-METHANE-LIKE PHOTOREARRANGEMENT OF DIPHENYL(PHENYLETHYNYL)BORANE-PYRIDINE*

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Abstract - The photorearrangement of diphenyl(phenylethynyl)borane-pyridine in benzene solution with irradiation at 254 nm leads to the formation of triphenylborirene(triphenylboracyclopropene), as evidenced by: a) the formation of α,α'-dideuterio-*cis*-stilbene upon treatment of the photolysate solution with DOAc; and b) the isolation of pentaphenylborole-pyridine from a photorearrangement conducted in the presence of diphenylacetylene. The triphenylborirene system was shown to be extremely sensitive to oxygen and to protic agents.

INTRODUCTION

Cyclic arrays of sp^2-hybridized boron and carbon atoms are systems of unusual interest, because the extent of carbon-boron *pi*-bonding should determine the relative aromatic character of the heterocyclic ring. Since an sp^2-boron center (R_3B) is isoelectronic with an sp^2-carbenium ion (R_3C^+), simple Hückel molecular orbital theory would predict that the borirene (**1**) and borepin (**3**) ring systems would possess aromatic stabilization,[3] as do their carbenium counterparts, the cyclopropenium[4] and the cycloheptatrienium ions.[5] Conversely, the borole ring system (**2**) would be expected to be destabilized and thus display antiaromatic character, similar to that shown by the cyclopentadienyl cation.[6] The syntheses of the mononuclear pentaphenylborole[7,8] (**2**) and heptaphenylborepin[8,9] (**3**) have confirmed the heightened reactivity of the former and the unusual stability of the latter. Such success has encouraged the hope that the unknown triphenylborirene (**1**) might draw upon sufficient aromatic stabilization to counter the strain inherent in the small ring. Previous attempts to form this borirene system, however, have been inconclusive.

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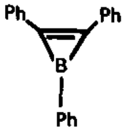
*Part VII in the series, "Bora-Aromatic Systems"; previous part: *J. Organomet. Chem.*, 1979, **171**, 141. This publication is dedicated to Professor Herbert C. Brown on the occasion of his 70th birthday. By his pioneering research with organoboranes, Professor Brown has deepened our understanding of steric effects and broadened the resources of organic synthesis.



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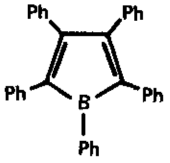

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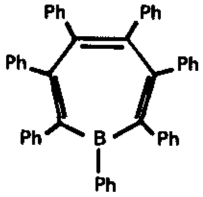
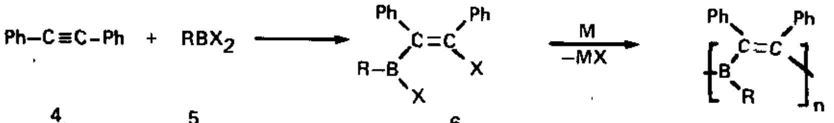


3

Thus, haloboration of diphenylacetylene (4) with RBX_2 (5), followed by dehalogenation of 6 with active metals, has led to systems of type 7, where the value of n is unknown (eq. 1):[10, 11]

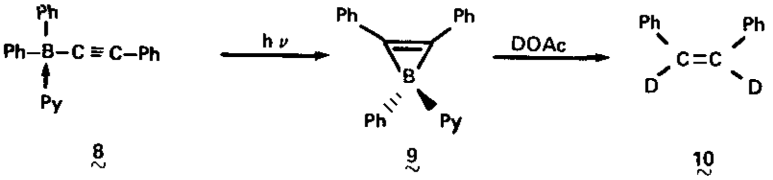


4 5 6 7 (1)

Cyclic dimers similar to type 7 (n = 2), namely 1,4-dibora-2,5-cyclohexadienes, have been identified as products from the action of monomeric BF on alkynes at elevated temperatures.[12] Because the synthetic approach depicted in eq. 1 employed such potent reactants as boron halides and metal reducing agents, any borirene (1) that might be generated had the strong possibility of undergoing subsequent cleavage reactions. Accordingly, we sought a route to the borirene that avoided strong reducing agents and Lewis acids. We now wish to report that such a route is the di-π-methane-like photorearrangement of diphenyl(phenylethynyl)borane-pyridine (8). Moreover, we have found it expedient to trap the triphenylborirene (1), once it has been formed, by interception with an alkyne.

RESULTS AND DISCUSSION

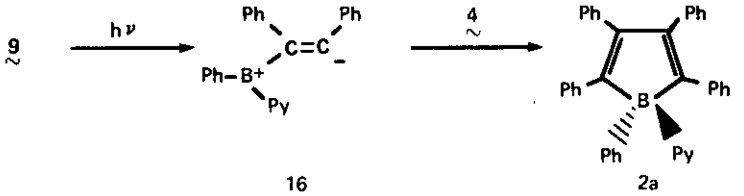
Our efforts to generate the borirene ring photochemically were modeled upon the known di-π-methane-like rearrangement of phenyl(triphenylmethyl)acetylene to tetraphenylcyclopropene.[13] Therefore, we synthesized diphenyl(phenylethynyl)borane-pyridine (8) from the interaction of diphenylboron bromide-pyridine and phenylethynyllithium.[14] Compound 8 in THF solution (under a nitrogen atmosphere) displays uv absorptions at 252.5 and 263 (sh) nm with log ε of 4.40 and 4.32, respectively. Irradiation of 1.02 g (2.95 mM) of 8 dissolved in 50 ml of anhydrous THF for 24 h in a Rayonet Reactor, Model RPR (low-pressure mercury lamps of 254 nm wavelength), and subsequent treatment of the photolysate solution with glacial O-deuterioacetic acid gave a 65% yield of an 18 : 1 mixture of *cis*- and *trans*-stilbenes (10 and 11). Aside from at least a 20% recovery of phenylacetylene, no other products were detectable. By mass spectral analysis, the *cis*-stilbene was composed of 49% dideuterated, 41% monodeuterated and 10% undeuterated hydrocarbon. On the other hand, the trans-stilbene was 12% dideuterated, 44% monodeuterated and 44% undeuterated. The integrated nmr spectrum of the cis-stilbene accorded with the presence of the deuterons on the vinylic positions. When a similar irradiation of 8 was conducted in anhydrous benzene solution, a comparable conversion to cis-stilbene was obtained, but no trans-stilbene was formed. The cis-stilbene was now ~95% dideuterated at the α,α'-vinylic positions (10), as shown by mass spectral and nmr analyses (eq. 2):



(2)

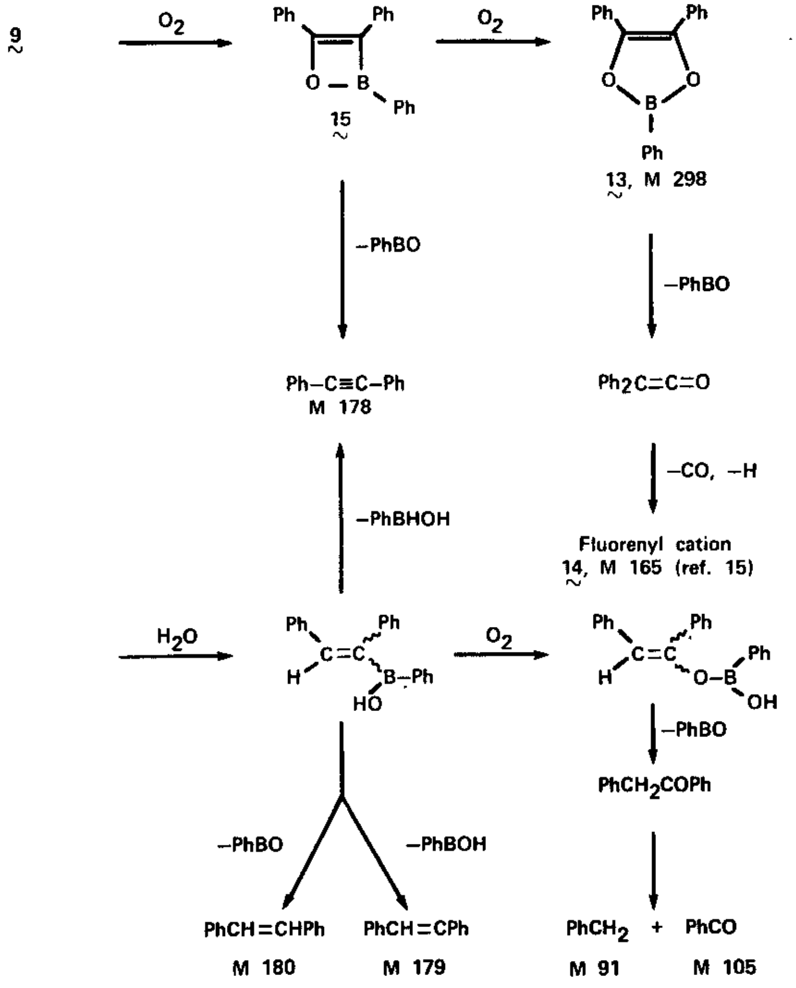
The expected photoproduct from a di-π-methane rearrangement of 8 would be the pyridine complex of triphenylborirene, namely 9. Isolation of the dideuterated cis-stilbene (10) is in accord with the formation of 9, but other precursors for 10 are possible. Any oligomer of 7 (n = 1, 2, 3 ...) would also yield 10 upon deuterolysis. Attempts to isolate the pure primary photoproduct without protolytic workup have failed because of the extreme air- and moisture-sensitivity of the organoborane intermediate. Direct isolation of the photoproduct under nitrogen by adding hexane to the benzene photolysate solution gave a cream-colored solid (12) melting over 90-100°C. Its ^{1}H nmr spectrum in CDCl$_3$ had multiplets at 7.9 (2 H, possible α-H of pyridine) and at 6.7-7.8 ppm (~18 H). Its acetolysis yielded only stilbenes 10 and 11 and its mass spectrum (70 eV) displayed only weak peaks corresponding to the presence of 9 (344 and 345 for ^{10}B and ^{11}B) or of 1 (265 and 266). Prominent mass peaks were exhibited at 310, 311 and 312 (trimer of PhBO), 298 (13), 180 (PhCH=CHPh), 179 (PhCH=CPh), 178 (PhC≡CPh), 165 (14), 105 (PhCO), 91 (C_7H_7), 89 and 88 (PhBH) and 79 (C_5H_5N). As depicted in Chart I, these mass peaks are consistent with oxidation and hydrolysis products arising from 9 during isolation or in the mass spectrometer. Confirmation that photoproduct 12 is extremely sensitive to oxidation was obtained by attempted purification of 12 by column chromatography on silica gel with hexane and chloroform as eluents. Benzil and diphenylacetylene were isolated, in addition to boron-containing material. Both organic products could readily have arisen from intermediates 13 and 15.[16]

In order to demonstrate that borirene 9 was the photoproduct from the photolysis of 8, therefore, we decided to capture 9 by means of diphenylacetylene (4). Irradiating an equimolar mixture of 8 and 4 in benzene solution led to the formation of at least 25% of pentaphenylborole as its pyridine complex, mp 179-181°C, as proved by mixture mp and a comparison of ir and nmr spectra (eq. 3):

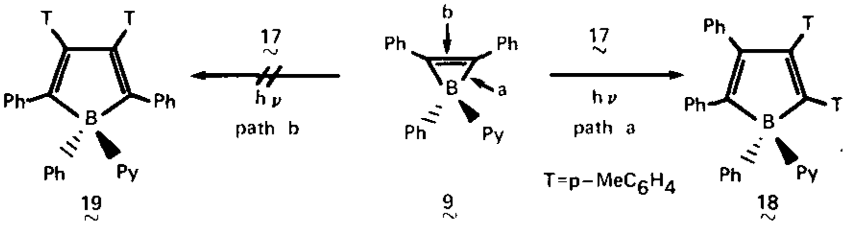


(3)

CHART I



The photochemical nature of the insertion of 4 into 9 was shown by generating 9 from 8 by irradiation and then heating 9 with 4 in the absence of light. Under these conditions, no borole was formed. Thus it would appear that the ring-opening of 9 to yield 16 is photo-promoted.[17] Intermediate 16 would then undergo a 1,3-dipolar cycloaddition to 4 or, in the absence of 4 and in the presence of THF, could abstract a proton from THF and isomerize. In this way, the monodeuterated and undeuterated *cis*- and *trans*-stilbenes would arise in the photolysis of 8 in THF solution. That the insertion of the alkyne into 9 took place at the carbon-boron bond (site a), rather than at the carbon-carbon bond (site b), was demonstrated by using di-p-tolylacetylene (17) as the trapping agent. Only borole 18 (~35%) could be detected in the reaction product. The identify of the borole as 18, rather than 19, was clear from the ^1H nmr spectrum, which displayed two different methyl signals of equal intensity at 2.20 and 2.25 ppm (downfield from TMS) and the expected ratios of α-pyridyl : aromatic : methyl protons of 2 : 26 : 6 (eq. 4):



(4)

In conclusion, the alkyne trapping experiments prove that the photolysis of 8 leads to the formation of borirene 9; no other oligomer of 7 could reasonably be considered as the precursor of boroles 2a and 18. Furthermore, borirene 9 has been shown to be extremely labile toward oxygen and toward protic agents. Therefore, if this unsolvated borirene (1) have any aromatic stabilization, such stabilization is clearly insufficient to prevent chemical attack on the carbon-boron bond.

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16. Analogous to the sensitivity of **9** to protolysis, even pentaphenylborole-pyridine (**2a**) undergoes methanolysis to yield methoxy(phenyl)-1,2,3,4-tetraphenyl-1,4-butadien-1-ylborane, mp 104.5-105°C, as verified by mass spectral and ^1H nmr analyses.
17. The rupture of **9** to yield singlet intermediate **16**, rather than a triplet intermediate, is suggested by analogy with the photo-cleavage of tetraphenylcyclopropene, which has been shown to yield a singlet open-chain intermediate (ref. 13).

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