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Preliminary communication

A boron containing analog of the norbornene ring system

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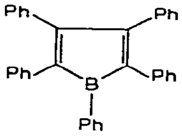
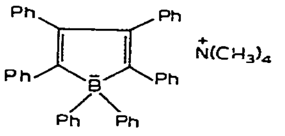
The recent report by Eisch and coworkers[1] on the synthesis of pentaphenylborole (I) prompts us to report our attempts to synthesize this compound and the related borate salt (II). Our interest in these compounds arose because of their potential usefulness as dienes in the Diels–Alder reaction to yield bridged boron-containing analogs of the norbornene and norbornadiene systems. We have recently postulated a bridged borate species to account for an unusual intramolecular rearrangement during the photolysis of potassium dimesityldiphenylborate[2].



(I)



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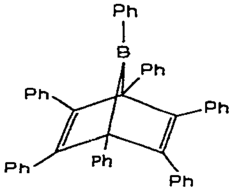
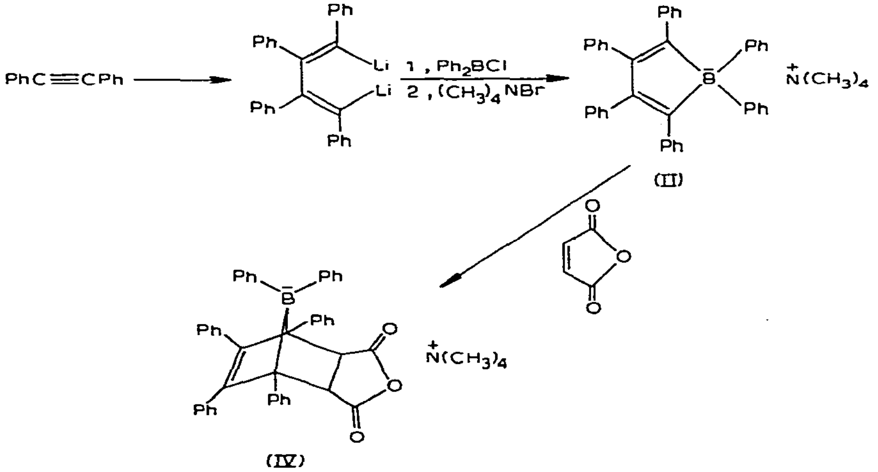


(III)

Like Eisch and his coworkers, we were unable to repeat the work of Braye, Hübel and Caplier[3], who prepared I by the reaction between 1,4-dilithiotetraphenylbutadiene and phenylboron dichloride in ether. The latter reagent is known to cleave ether rapidly at room temperature[4]. We therefore replaced the ether used in the preparation of the dilithio derivative with benzene, prior to the addition of the phenylboron dichloride in dry benzene. Frequently, after work-up of the reaction products, we observed peaks in the mass spectra of parent ions corresponding to hexaphenylbenzene and its dihydro derivative. Since the preparation of the dilithiobutadiene derivative from diphenylacetylene proceeds in only approximately 70% yield, we suspected that the excess unreacted acetylene was adding to the unstable borole (I) to yield the bridged boron analog of a norbornadiene derivative III. Thermally this could yield hexaphenylbenzene, or in the work-up a dihydro derivative could result. We attributed our failure to isolate I to its apparent reactivity due to its antiaromatic character; we consequently directed our attention to the tetrahedral borate derivative II. This derivative should behave like a diene and show similar stability to dialkyldiaryl borate salts.



We have found that the borate II can be prepared in 70% overall yield from diphenylacetylene by the route indicated in Chart 1. The tetramethylammonium salt II crystallized from acetone/water as pale yellow needles, m.p. 227–230°, λ_{max} (MeCN) 362 nm (ϵ 9250). (*Anal.*: Found: C, 88.6; H, 7.1; B, 1.7; N, 2.3. $C_{44}H_{42}BN$ calcd.: C, 88.6; H, 7.0; B, 1.8; N, 2.4%). The NMR spectrum (acetone-d_6) showed a ratio of 12 tetramethylammonium protons to 30 aromatic protons. The mass spectrum showed a parent ion at *m/e* 536 and a strong *m/e* 59 peak. This corresponds to loss of trimethylamine and transfer of a methyl with cleavage of a B–C bond to yield $(C_6H_5)_2B{-}C(C_6H_5){=}C(C_6H_5){-}C(C_6H_5){=}C(C_6H_5)CH_3$.

The borate salt II undergoes a facile Diels–Alder reaction with a number of π-electron-poor dienophiles. For example, when equimolar acetone solutions of II and maleic anhydride are mixed, a quantitative yield of the stable bridged borate IV results within seconds.

The tetramethylammonium 7-diphenylboratobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (IV), which was precipitated with ether, melted at 185° (dec.). (*Anal.*: Found: C, 83.3; H, 6.6; B, 1.4; N, 2.0. $C_{48}H_{44}BNO_3$ calcd.: C, 83.1; H, 6.3; B, 1.5; N, 2.0%). The NMR spectrum (acetone-d_6) showed singlets at δ 3.17 (12H) and 4.58 (2H) and complex absorption centered at 7.2 ppm (30H). The IR spectrum showed the characteristic anhydride C=O bands at 1780 and 1830 cm^{-1} and a strong band at 955 cm^{-1} which is present in the spectra of various tetramethylammonium salts.

Similarly, *N*-phenyl and *N*-(α-pyridyl)maleimide react with the borate II to yield Diels–Alder adducts as judged by spectroscopic and analytical data.

The bridged borate IV is stable to air and the anhydride ring is stable to methanol under reflux for 3 h. Like other borates[5], the system is unstable to acid, but we have been unable to resolve the mixtures obtained from the acid hydrolysis.

Although Eisch and his coworkers included a diagram of the bridged bora derivative (III) in their paper, no discussion concerning this structure was given. To our knowledge the borate compound IV is the first example of a boron-containing analog of a norbornene derivative. Like other bridged organometallic analogs of the norbornane system, the bora and borate compounds are possible precursors of divalent boron species - analogs of carbene[6]. In fact, the hexaphenylbenzene reported by Eisch and observed by us may have arisen by elimination of a divalent phenylboron species from the bridged intermediate (III).

In connection with our photochemical studies, we are investigating the synthesis and reactions of bridged boron compounds and their possible use as generators of divalent boron species.

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