The borylation of aromatic compounds by
dehalogenation products of
dialkylamino(dihalogeno)boranes

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Abstract - Reactions of subvalent boron species, generated by the dehalogenation of R2BNX2 (X = Cl, F; R = Pr or Bu) by Na/K, with aromatic compounds in 1,2-dimethoxyethane lead to polycyclic species in which formal borenene units, "BNR2" are added across or inserted into the carbon skeleton of the aremate.

The highly reactive borenene or borenoid intermediates lead to complex product mixtures and lossy high vacuum distillations make it difficult to evaluate the true yields of the respective products. In some cases (compounds 9 and 13) pure isolated material came up to nearly 50%. Structures have been deduced from MS and NMR (1H, 11B, 13C and in part 15N) data as well as by x-ray structure analyses for 14 of the 27 species formulated. Formation of specific compounds depends on the reaction conditions (see the references cited). All species exhibit high thermal stability, some are slowly hydrolysed by atmospheric moisture while others are stable to wet acetone for prolonged periods. With one exception (9), the novel species are quite different from carbonboranes.

INTRODUCTION
Carbenes, derivatives of divalent carbon are six electron species. They can be described as Lewis acids and (in their singlet state) as Lewis bases at the same time. Without a suitable reaction partner, carbenes will polymerize. With aromatic compounds carbenes will react either by 1,2-addition across a (CC) double bond thus forming norcaradiene derivatives or by insertion into the carbon skeleton thus forming e.g. cycloheptatriene. Cases where the same aromatic ring reacts with two carbone species are extremely rare. A borenene is a derivative of monovalent boron and therefore a four electron species. Even its electron deficiency may be diminished by π-donor substituents its reactivity must be higher than that of a carbone.

To be certain that a free borenene is acting as the reaction partner to any substrate, the borenene has to be generated either in a gas phase reaction or in solution by elimination from cyclic moieties. This has been performed by Timms by the high temperature preparation of boron monohalides and their reaction with alkynes to give 1,4-dihalo-1,4-dibora-cyclohexadienes (ref. 1). When borenenes are generated in solution, by the dehalogenation of dihaloboranes, RBX2, with active metals, reaction products obtained can be formed also by radical reactions of borenoids, RBX, and a subsequent second dehalogenation step. Surprisingly no attempts have been made to react subvalent boron species (borenenes or borenoids) with aromatic compounds in the past. - However the borole dianion A has been reacted with CH3BBr2 to yield the 2,3,4,5-tetracarba-nido-hexaborane(6) derivative B, while with PrlNBC12 the 2,6-diborabicyclo[3.1.0]hex-3-en derivative C is obtained (ref. 2). Like in the 1,4-dihalo-1,4-diboracyclohexadienes classical, cyclic structures are stabilized by the diminution of the electron deficiency at the boron atoms by additional π-bonding from their substituents.

All species marked by letters (denoting the work of others) or by numbers (our work) are depicted in Table 1. All these compounds have been fully characterized by their mass-(MS) and NMR (1H, 11B, 13C and in part 15N) spectra. Those labeled with an * have been substantiated by x-ray structure analyses.

RESULTS AND DISCUSSION
By the reaction of X2BNPr2 (X = Cl or F) with Na/K and C6H6 in (CH3OCH2)2, species C6H6* xBN(l-Pr)2 (x = 1-6) are formed as shown by field ionization (FI) mass spectrometry.

\[ x = 10 - 0.1; \ y = 1 - 6; \ X = \text{Cl, F; } R = \text{Pr}, \text{Bu}^1 \]
By fractionating high vacuum distillation of the viscous mixture of the reaction products, so far three bicyclic species containing two (1) and three (2, 3) formal borene units "BNPr₂" have been isolated (ref. 3, 4). In all these products two double bonds are retained; 3 is a spirocyclic species and hydrogen transfer is observed. The structure of 4 (which is obtained from 1,4-dilisopropyl-benzene) presents the same skeleton as 1, while 5 derived from toluene corresponds to 2. Likewise the reaction product of p-xylene with two "BNPr₄" units, 6 and compounds 7 and 8 which originate from 1,2,4-trimethylbenzene and N-dimethyl(4-trimethylsilyl)aniline belong to a common type of structure (ref. 5). The type of skeleton which is presented by the compounds 6 to 8 seems to be easily formed and is also contained in 9 which is the main product formed in the dehalogenation of X₂BNPr₄ by the naphthalene alkali-metal complex in glyme (ref. 3, 6, 7). These products apparently are formed by the 1,4-addition of a "borene" unit across a six membered aromatic ring and by insertion of the other "borene" under ring enlargement. Again compounds 2 and 4 still contain one part of the remaining aromatic ring into the bonding system of the borylated part of 9 apparently stabilizes the aromatic ring against further attack. The reaction product obtained from m-xylene by the addition of two "borene" units represents a tricyclic structure 10 characterized by a six- and a five membered ring with boron atoms and a cyclopropane unit (ref. 8). The species 11 obtained from toluene contains four "borene" units and consists of a seven- and two five membered ring (ref. 8). Compounds 12 and 13 made from toluene and tert-butylbenzene consist of each a seven-, a six- and a five membered ring (ref. 5). The compounds 11 - 13 still contain one double bond in the seven membered C₂C₇ ring.

So far the species C₈H₆ · BNPr₂ and C₇H₆ · 6 BNPr₂ (or derivatves thereof) have not been isolated. This is due to the fact that the products with just one "borene" oligomerize rapidly and perhaps are less stable than species containing additional boron atoms. From the dianion of cyclooctatetraene (a 10 π-species) however 17 has been isolated, which would suggest that a 1,4-addition is the first step of the reaction. However from FI-MS and ¹³C-NMR it must be concluded, that also a second species with the same mass is formed, containing the "borene" between two C-atoms with sp²-geometry (ref. 10). On the other hand 18 is apparently the main product with acenaphthylene, a species were no 1,4-addition between two (CH) groups is possible (ref. 6). Also it shows that 1-methylnaphthalene is extremely difficult to be borylated, while 2-methylnaphthalene easily adds up to five boron units (ref. 5). C₇H₆ · 6 BNPr₂ has not been obtained in pure state so far.

According to the structural data obtained, substitution by boron appreciable lengthens the C-C bonds, so in 11 a (CC) bond which is substituted by 3 boron atoms is 159.6 pm, the bond between two C-atoms carrying boron atoms is 164.2 pm long (ref. 8). The two (CC) bonds in 6, prepared from Pr₂NB(C₁)-CH=CH-B(C₁)NPr₂ with Na/K and phthalocyanine palladium catalysis, are 163 and 169 pm long (both between C-atoms of sp³-geometry which together carry four B atoms) (ref. 11). The (BC) bond lengths are between 158 to 160 pm like those in other 3-dimensional boron carbon structures with classical bonding obtained recently by different methods (ref. 11, 12). Compounds 1 - 18 contain only three coordinated boron and three- or four coordinated carbon (sp² and sp³ hybridization) and therefore are different from carboranes. The same is true for 19 which is obtained from norbornene and represents an uncomplexed 1,2,3-triborolone derivative (ref. 5; see also ref. 13). If however norbornadiene is the starting material, C₇H₆ is eliminated from the reaction product in a retro Diels-Alder reaction and the corresponding 1,5-dicarba-closo-pentaborane(5) derivative 20 is formed (ref. 5). 20 has not to different structural parameters compared to 1,5-dicarbo-closo-pentaborane(5) and its alkyl derivatives (ref. 14, 15), however quite different NMR-data indicating that 20 is rather to be described as a classical bonded system.

Benzenes react with difluorosilylene to give a compound in which cyclohexadiene is bridged in 1,4-position by a difluorosilylene trimer (2,2,3,3,4,4-hexafluoro-2,3,4-trisilacyclo[3.2.2]nona-6,8-diene) (ref. 16). This resembles the structure of 19. Also 21, the product of the reaction of the alkali metal complex of 2,2'-dipyridyl and C₃B₂BNPr₂ (ref. 17), corresponds to a species recently obtained from photolytically generated di-tert-butylsilylene and 2,2'-dipyridyl (ref. 18).

If aromatic compounds are used which show restrained reactivity towards the subvalent boron species generated, the "borene" species will attack the solvent, 1,2-dimethyethane, and diborylated ethyne 22 is formed under partial hydrogenation of the aromatic compound (ref. 6, also see ref. 19).

Furtheron the reaction of subvalent boron species has been studied with oxygen-, sulfur- and nitrogen heterocycles (ref. 20, 21). For example with benzothiazole compounds 23 and 24 have been isolated (ref. 20). From 2-methylbenzoxazole besides of (PhH)₂BNPr₂ and (PrN)₂B-C≡N compound 25 has been isolated and the formation of 26 and 27 substantiated by MS and NMR-spectroscopy (ref. 20). Subvalent boron compounds generated by active metal dehalogenation of dithiogene- or diorganylaminoboranes are by far more reactive than carbenes. Even the formation of a free boron species "BNPr₂" in these systems cannot be substantiated unambiguously, products obtained support this assumption.
Certainly it would be of high interest to make use of todays facilities of structural characterization for the only example of a transition metal borene complex, \((\text{CO})_4\text{FeBNMe}_2\), described 20 years ago (ref. 22).

### TABLE 1

Letters denote compounds described by other authors. Numbers denote our own results. Compounds labeled with an * have been characterized by x-ray structure analyses.

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<th>Number</th>
<th>Compound Structure</th>
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<td>3</td>
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<td>(Bu$_2$N)$_2$B=C=N</td>
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REFERENCES

5. A. Meller et al. unpublished results.