THE ADDITION OF METHYLBORYLENE TO ACETYLENES

SYNTHESIS OF 1,4-DIBORACYCLOHEXA-2,5-DIENES, AND OF A BORIRENE AND A DIBORETENE DERIVATIVE

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Abstract—The synthesis of 1,4-dimethyl-2,3,5,6-tetra-*n*-alkyl-1,4-diboracyclohexa-2,5-dienes from the reaction of di-*n*-alkylacetylenes with the methylborylene-generating system $2C_8K/MeBBr_2$ is described. A mechanism for these reactions is proposed. The addition of methylborylene to di-*t*-butylacetylene results in the formation of 1-methyl-2,3-di-*t*-butylborirene and of 1,3-dimethyl-2,4-di-*t*-butyl-1,3-diboretene.

The concept of three-membered heteroaromatic compounds was broached in 1962 by Volpin *et al.*;[1] in their pioneering paper they suggested as a route, possibly leading to these compounds, the addition of carbene analogues to acetylenes. Further, they made an outline of species that might qualify as carbene analogues and suggested a number of their possible reactions. In their publication the potential aromaticity of borirene (I) is first mentioned.

Thus, according to Volpin *et al.*,[1] addition of a borylene to an acetylene might yield a borirene (I):
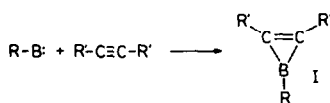
Both possibilities, generating a borylene and synthesizing a borirene derivative have intrigued chemists in the years following.

Kuchen and Brinkmann[2,3] treated phenylboron dichloride with sodium in toluene, to obtain polymeric $[PhB]_n$. The suggestion that in this way, by abstraction of the halogen atoms from $PhBCl_2$, phenylborylene might have been generated was

made in 1966 by Nefedow and Manakow.[4] Köster and Grassberger[7] treated ethylboron difluoride with lithium in THF, to obtain carboranes.

In 1967 Eisch and Gonsior[8] presented indirect chemical evidence for the initial formation of the borirene ring in solution. They did not generate a borylene, but chose a route involving reductive ring closure of the haloboration product of diphenylacetylene (Fig. 2). The compounds in square
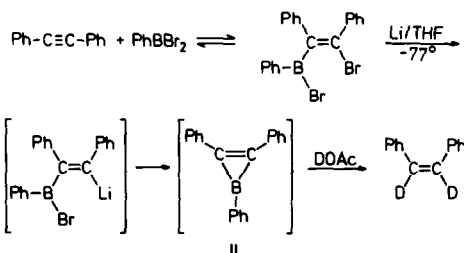
brackets were not isolated. The occurrence of triphenylborirene (II) was inferred from the product obtained upon deuteroacetolysis. It should be noted that the formal dimer of triphenylborirene, hexaphenyl-1,4-diboracyclohexa-2,5-diene (III, hexaphenyl-DBCH) would yield the same acetolysis product (Fig. 3). The DBCH structure (III)

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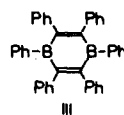
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was postulated by Lappert *et al.*[5] in analogy to the products of similar reactions with silylenes and germylenes.[4]
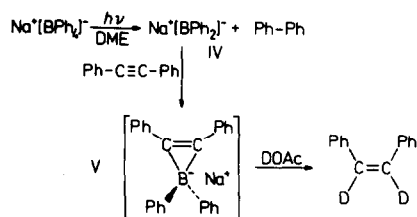
Timms[9-11] obtained high yields of boron monofluoride, or fluoroborylene, by passing boron trifluoride over crystalline boron at 2000° under low pressure. The short-lived BF was made to react with acetylenes by co-condensation. In this way 1,4-diboracyclohexa-2,5-diene (DBCH) derivatives were formed; no trace of the expected borirenes was found. Timms supposed that the borirene formed immediately dimerized to the corresponding DBCH derivative. By cracking B_2Cl_4 at 1100°

Timms was able to produce BCl, chloroborylene,[11] which reacts with acetylenes in the same fashion as BF.[9-11] Timms found the [FBC_4R_4BF] and [$ClBC_4R_4BCl$] species isolated to be planar. Contrary to this, the compounds [$EtBC_4Et_2R_2BEt$] reported in 1966 by Binger[12] were concluded to have a non-planar carborane structure. These compounds, however, were synthesized along a totally different route (Fig. 5). For R=Et the following *nido*-carborane structure was proposed:

Lipscomb *et al.*[13] compared the geometries of the possible isomers of [HBC_4H_4BH] and [FBC_4H_4BF] by means of PRDDO calculations. For [HBC_4H_4BH] the carborane structure appeared to be more stable (by 9 kcal/mole) than the planar isomer. Placing electron-rich substituents on the boron atoms proved to stabilize the planar structure: planar [FBC_4H_4BF] was found to be

43 kcal/mole more stable than the carborane isomer, thus confirming the conclusions drawn by Timms.[10]

In 1975 Eisch *et al.* reported[14] borylene character for the diphenylborate(I) anion (IV). When sodium tetraphenylborate was irradiated in DME in the presence of diphenylacetylene, subsequent acetolysis yielded (among other products) *cis*-stilbene, the formation of which was ascribed to the intermediate occurrence of the diphenyl-(diphenylvinylene)borate(III) anion (IV), a species possessing a borirene nucleus (Fig. 7).

Nöth *et al.*[15,16] synthesized 1-bora-4-stannacyclohexa-2,5-diene derivatives via hydrostannation of dialkinylboranes (Fig. 8). However, exchange of tin by boron, to yield a DBCH derivative, failed. A slightly different route was followed by Herberich and Hessner,[17,18] leading to DBCH derivatives (Fig. 9).

In 1979 Eisch and Becker[6] reported on another attempt to generate borylenes by abstracting the halogen atoms from organoboron dihalides by suitable reducing agents and, subsequently, to trap the borylenes with diphenylacetylene to produce a borirene. No positive results were obtained.

Bock *et al.* published a study[19] of the He(I) photoelectron spectrum, the one electron-reduction behaviour and the electronic structure of 1,4-difluoro-2,3,5,6-tetramethyl-1,4-diboracyclohexa-2,5-diene, in comparison to the isoelectronic duroquinone.

A theoretical study of (amongst others) the

borirene system was published by von Schleyer *et al.*[20] (*vide infra*).

With DBCH derivatives a number of transition metal sandwich complexes have been synthesized; those marked with an asterisk have been characterized by X-ray analysis: $(FBC_4Me_4BF)Ni(CO)_2^*$, $(FBC_4Me_4BF)_2Ni^*$, $(FBC_4Me_4BF)Co(C_5H_5)$, $(FBC_4Me_4BF)Fe(CO)_3$, $(FBC_4Me_4BF)Ni(cyclo-octa-1,5-diene)$,[21,22] $(MeOBC_4H_4BOMe)_2Ni$,[18] and $(MeBC_4H_4BMe)Co(C_5H_5)^*$.[23] Due to the fact that in the crystals of $(FBC_4Me_4BF)Ni(CO)_2$ molecules of free $[FBC_4Me_4BF]$ were present, the structure of the latter was determined as well.[22]

Herberich *et al.* reported the synthesis and structure determination of a triple-decker sandwich complex with DBCH as a bridging ligand: $(C_5H_5)Rh(MeBC_4H_4BMe)Rh(C_5H_5)$,[24] and the He(I) photoelectron spectrum and the electronic structure of the sandwich complex $(MeBC_4H_4BMe)Co(C_5H_5)$.[25]

Recently, Eisch *et al.* stated[26] that irradiation of diphenyl(phenylethynyl)borane-pyridine (**VI**) in THF or benzene leads to the formation of the pyridine complex of triphenylborirene (**VII**) (Fig. 10). Eisch *et al.* did not isolate (**VII**) but its
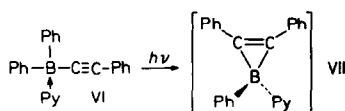
occurrence was inferred from the products obtained upon treatment of the reaction mixture (in benzene) with deuteroacetic acid and upon irradiation of a mixture of (**VI**) and diphenylacetylene in benzene. In the latter reaction the pyridine complex of pentaphenylborole was produced (Fig. 11). The borirene complex (**VII**) was reported to be extremely labile towards oxygen and protic agents.

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†Parts of this work were published in preliminary publications.[29,30]
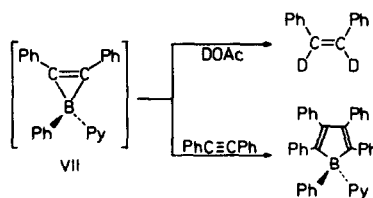
This was ascribed to a lack of aromatic stabilization. It is evident that hardly any degree of aromaticity is to be expected in a Lewis base adduct of a borirene, as in such a complex the boron atom is 4-coordinated and thus cannot provide an empty *p* orbital to partake in the π electronic system.

In a recent publication[27] Herberich and Hessner described the synthesis of the 6π-electron system $[FcBC_4H_4BFc]^{2-}$ ($Fc=(C_5H_5)Fe(C_5H_4)$), obtained by reduction of $[FcBC_4H_4BFc]$ by sodium amalgam. Further, a number of transition metal sandwich complexes of this DBCH, and nucleophilic substitution reactions on these complexes were reported.[27,27a]

It occurred to us that most attempts to synthesize a borirene by addition of a borylene to an acetylene had been undertaken using diphenylacetylene as a substrate. As it is to be expected that borylenes have an even more electrophilic character than carbenes, acetylenes with electron-donating groups, in our opinion, should offer better chances of trapping a borylene than diphenylacetylene. In view of our earlier finding that the system $2C_8K/MeBBr_2$ is a suitable methylborylene generator,[28] it was decided to study the reactions of methylborylene with dialkylacetylenes.†

RESULTS

In Table 1 the results of the reactions of the system $2C_8K/MeBBr_2$ with various acetylenes are summarized.

When diphenylacetylene was subjected to the system $2C_8K/MeBBr_2$ in boiling cyclohexane, inspection by ^1H NMR showed that no reaction had

Table 1. Identified products of the reaction of the system $2C_8K/MeBBr_2$ with various acetylenes

acetylene	major product	benzene derivative	other products
Ph-C≡C-Ph	no reaction		
n-Bu-C≡C-n-Bu	DBCH (1 isomer)	$n\text{-}Bu_6$-benzene	
n-Pr-C≡C-n-Pent	DBCH (2 isomers)	$n\text{-}Pr_3\text{-}n\text{-}Pent_3$-benzene	
Et-C≡C-n-Hex	DBCH (2 isomers)	$Et_3\text{-}n\text{-}Hex_3$-benzene	
t-Bu-C≡C-t-Bu	borirene + 1,3-diboretene		
Me-C≡C-Me	carborane (1 isomer)		$[C_2Me_2]_2[MeB]_4 + [C_2Me_2]_3[MeB]_4$
Et-C≡C-Et	DBCH + carborane (both 1 isomer)		

taken place. After filtering off all solid material and removal of all volatile components, the residue was subjected to GC/MS. Only diphenylacetylene could be detected. No 1-methyl-2,3-diphenyl-borirene or 1,4-dimethyl-2,3,5,6-tetraphenyl-1,4-diboracyclohexa-2,5-diene had been formed (thus confirming the results of Eisch and Becker[6]), but no haloboration products[6,8] either.

Next, di-*n*-butylacetylene (5-decyne) was chosen as a substrate. The reaction with the system $2C_8K/MeBBr_2$ was carried out in boiling benzene. In the course of hours, inspection by ^{1}H NMR showed that reaction had taken place and the potassium–graphite turned black. When no further change in the ^{1}H NMR spectra was observable, the solid material was filtered off, the volatile components were removed *in vacuo* and the residue was subjected to vacuum fractionation. The fractions collected were investigated by GC/MS. It appeared that a DBCH derivative, 1,4-dimethyl-2,3,5,6-tetra-*n*-butyl-1,4-diboracyclohexa-2,5-diene (VIII), had been obtained in a pure state. No trace of the expected borirene was present; neither were halo-boration products found (Fig. 12). Compound
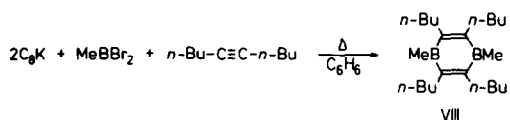
(VIII) is a viscous yellow liquid, boiling at 60–65°/10^{-6} Torr, highly reactive towards air and water. The reaction was carried out in cyclohexane as well, to yield the same results.

If DBCH's are formed via the direct dimerization of borirenes, this reaction can be described by either or both of the following two mechanisms. Starting from an asymmetric acetylene, different
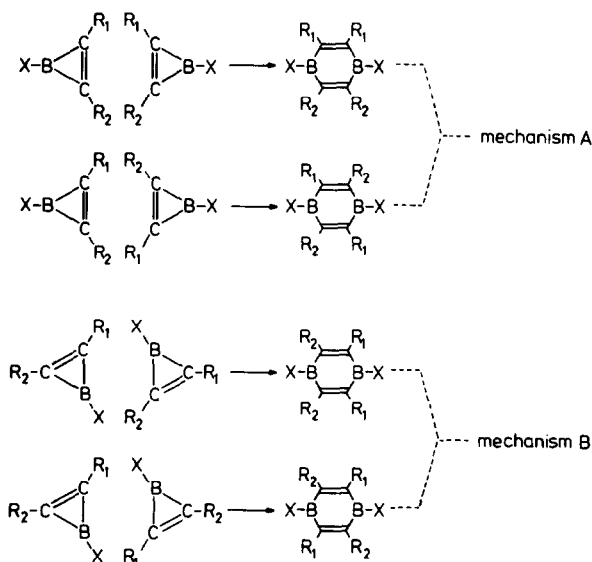
products will be obtained by either mechanism (Fig. 13).

It should be noted that the second and the fourth product are identical. A variation of mechanism *B* is a reaction course in which 1,2-dibora-cyclohexa-3,5-dienes are formed (mechanism *C*, Fig. 14). It is seen that, using an asymmetric
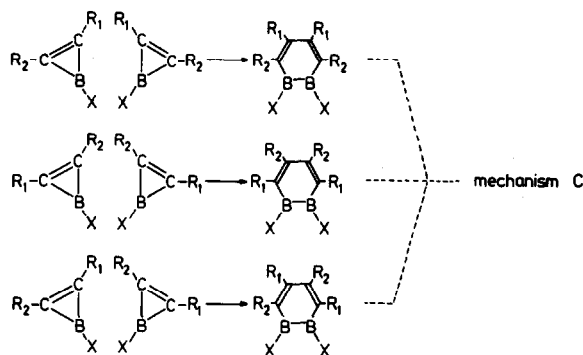
acetylene, both mechanism *A* and *B* yield two distinct products. Mechanism *C* yields three isomers. In one of his experiments with BF, Timms used propyne as a substrate.[10] He obtained three 1,4-DBCH's (one of them in a trace quantity), but no 1,2-DBCH's (Fig. 15). Compound (IXa) can
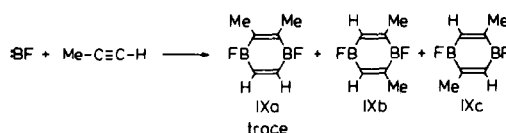
only stem from mechanism *A*, (IXb) only from mechanism *B*, and (IXc) from both *A* and *B*.

In order to get insight into the matter, the system $2C_8K/MeBBr_2$ was reacted with *n*-propyl-*n*-pentylacetylene (4-decyne). GC/MS investigation of the reaction mixture showed that two DBCH isomers had formed, with almost identical mass spectra, in a relative ratio of 1:2.6. No borirene was detected. The same experiment, carried out with ethyl-*n*-hexylacetylene (3-decyne) showed, upon GC/MS investigation, that two DBCH derivatives had formed, again with very similar mass spectra, in a relative ratio of 1:3.0. Again, no borirene was found.

In our opinion, acetolysis of the products of the reaction of methylborylene with an asymmetric acetylene should offer a possibility of deciding between mechanisms *A*, *B* and *C*. Timms did not observe a general pattern in the hydrolysis products of his DBCH's,[10] viz:

$$BF + CH\equiv CH \rightarrow \xrightarrow{H_2O}$$

90% ethene + 10% 1-butene

$$BF + MeC\equiv CH \xrightarrow{\text{H}_2\text{O}} \longrightarrow$$

complex mixture of hexenes with
ca. 10% propene

$$BF + MeC\equiv CMe \xrightarrow{\text{H}_2\text{O}} \longrightarrow$$

3,4-dimethyl-2-hexene with
a little cis-2-butene.
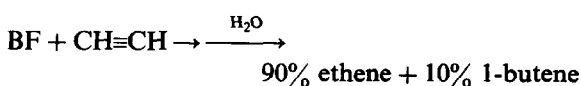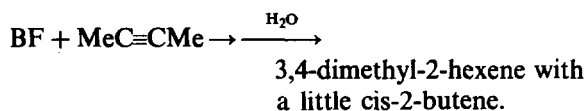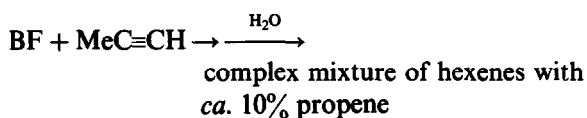
Timms supposed that hydrolysis was accompanied by polymerization. Acetolysis (with glacial acetic acid) of the crude mixture obtained upon reaction of $2C_8K/MeBBr_2$ with ethyl-*n*-hexylacetylene (3-decyne) yielded only 3-decene (according to GC/MS), thus accounting for mechanism *B*. Neither 3-hexene nor 7-tetradecene could be detected, so mechanism *A* could be ruled out. A C_{20}-olefin was not found either, so mechanism C could be excluded as well.

Of course, formation of a DBCH molecule by two borirene molecules might be preceded by ring opening of the borirenes, leading to biradicals. However, combination of the biradicals would, in our opinion, result in the formation of a large amount of polymeric material (apart from the formation of 1,4-DBCH and, possibly, 1,2-DBCH) which, in turn, would yield dienes upon acetolysis (Fig. 17). Dienes were never found upon acetolysis of crude reaction mixtures. Further, it is to be expected that a biradical would react with a molecule of acetylene to yield a borole. Boroles were never encountered in the reaction mixtures.

In the case of the formation of DBCH's from asymmetric acetylenes, the preponderance of one

isomer over the other (especially as the substituents show a larger difference in size) can be explained

in terms of steric hindrance. In the dimerization of the asymmetric borirene (XI), DBCH (XIIa) is expected to be favoured over DBCH (XIIb), both on grounds of easier approach of the reactants and less steric hindrance in the product (Fig. 18). Compound (XIIa) can be formed in a second way; here, howe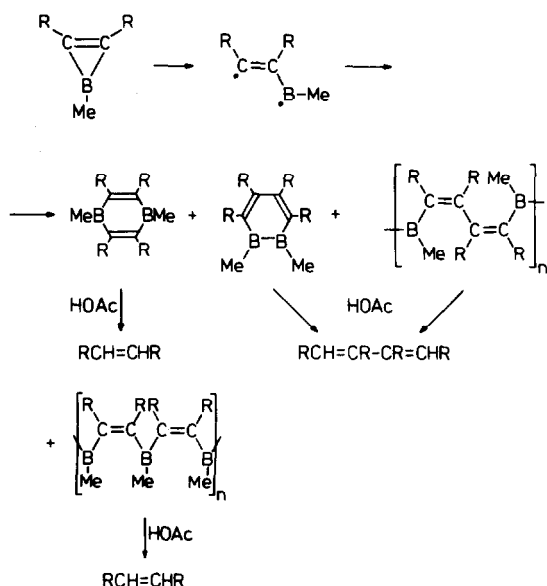ver, the approach is even more unfavourable (Fig. 19). These effects are expected to be more evident in the ratio of the products of the
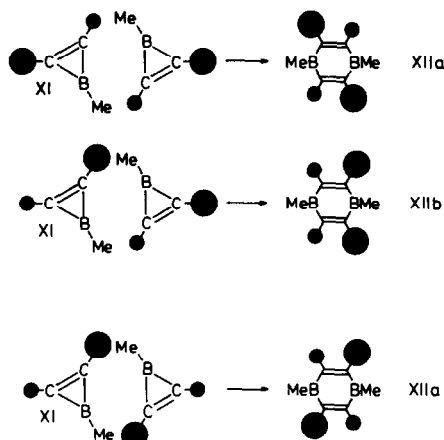
reaction of methylborylene with ethyl-*n*-hexylacetylene than with *n*-propyl-*n*-pentylacetylene, and, in fact, this was observed experimentally.

In personal discussions Prof. von Schleyer[31] suggested the use of an acetylene with very bulky substituents, since this might render the formation of a DBCH derivative impossible on two counts. First, in the DBCH molecule itself the steric hindrance might be so extensive, as to make the formation of the species thermodynamically unfavourable. Second, if DBCH is formed from the direct reaction of two molecules of borirene, a close approach of the two molecules could be impeded by the bulky substituents. Thus the reaction might halt at the stage of the borirene derivative.

It was decided to use di-*t*-butylacetylene (2,2,5,5-tetramethyl-3-hexyne) as a substrate, especially as the electron-donating properties of the tertiary butyl groups might impart an extra stability to the borirene molecule. Reactions were carried out between C_8K, $MeBBr_2$, and di-*t*-butylacetylene in benzene, both at reflux and at ambient temperature. The reactions were followed with ^{1}H NMR; it was necessary to use sweep widths down to 0.2 ppm in order to be able to distinguish between the various *t*-Bu signals, as the differences in chemical shifts between reactant and product(s) were very small. After work-up (see Experimental Part) the results of the reactions were

studied by GC/MS. No 1,4-dimethyl-2,3,5,6-tetra-*t*-butyl-1,4-diboracyclohexa-2,5-diene was found at all; instead, in both reactions a product had formed, the mass spectrum of which pointed to 1-methyl-2,3-di-*t*-butylborirene (XIII).

In both reactions, but especially in the one that had been carried out at room temperature, a second compound was present the fragmentation and isotope pattern of which pointed to the compound *t*-Bu$_2$C$_2$(BMe)$_2$ (XIV), the product of the reaction of two methylborylene units with one molecule of di-*t*-butylacetylene, a diboretene (Fig. 20). For the diboretene (XIV) several structural

$$2C_8K + MeBBr_2 + t\text{-Bu-C}{\equiv}\text{C-}t\text{-Bu} \xrightarrow[C_6H_6]{(\Delta)} \underset{\substack{\text{B}\\|\\ \text{Me}\\ \text{XIII}}}{\overset{t\text{-Bu}\diagdown\diagup t\text{-Bu}}{\text{C}{=}\text{C}}} + t\text{-Bu}_2C_2(BMe)_2$$

XIV

formulae can be envisaged: two 1,3-diboretenes (XVa and XVb, of symmetries D$_{2h}$ and C$_{2v}$ respectively), one diborabicyclo[1.1.0]butane (XVI) and one 1,2-diboretene (XVII):

Extensive calculations on the aromaticity in hypothetical small rings containing boron and

carbon ([CH]$_2$[BH]$_n$, n = 1,2) have been carried out by von Schleyer *et al.*[20] It was predicted that the 1,3-diboretene [CH]$_2$[BH]$_2$ with the structure of compound (XVb) would be the most stable. In this puckered molecule (symmetry C$_{2v}$) the C–C distance is calculated to be extremely large (1.858 Å); the two extra valence electrons are found to remain delocalized over the entire ring. The angle between the planes defined by B$_1$C$_1$C$_2$ and C$_1$C$_2$B$_2$ is predicted to be 125.1°. The structures corresponding to (XVa) (symmetry D$_{2h}$) and (XVI) are not even local minima. The 1,2-diboretene (XVII) is calculated to be 7–17 kcal/mole higher in energy than the puckered 1,3-diboretene (XVb).

In the mass spectrum of (XIV) (*vide infra*) a fragment is found with half the molecular mass, with an intensity of 34%. In our opinion, this mass represents the fragment *t*-BuCBMe$^+$, originating

from cleavage of the four-membered ring in a 1,3-diboretene (XVa or XVb). Fragmentation of the four-membered ring of the 1,2-diboretene (XVII) is not expected to proceed via C=C bond cleavage. Rather, cleavage of the B–C bonds should occur, to produce fragments *t*-Bu$_2$C$_2$$^+$ and/or Me$_2$B$_2$$^+$ (or MeB$^+$). These fragments were not found.

Our assignment of the 1,3-diboretene structure to (XIV) in preference to the 1,2-diboretene structure (XVII) is in accord with the results of the calculations by von Schleyer *et al.*[20]

The quantity of diboretene formed in the reaction carried out at reflux temperature was quite small as compared to the quantity of borirene (GC/MS, NMR). 1-Methyl-2,3-di-*t*-butylborirene (XIII) appears to be thermally quite stable, taking into account that in the course of one of its syntheses a reflux period (in benzene) of 24 hr was included, and that benzene could be removed from it by distillation under atmospheric pressure without noticeable decomposition. This is borne out by its calculated[20] resonance energy of 70–75% of that of its carbocation analogue (*cf.* the resonance energy of 1-methylborepin, which was calculated by us to be 75–85% of that of its analogue, the tropylium cation[36]).

Mass spectra

The mass spectra (electron impact) of the DBCH derivatives, synthesized starting from 3-decyne, 4-decyne, and 5-decyne are fairly complex. The base peak is always found at *m/e* 41 ([Me$_2$B]$^+$). The parent peaks (with intensity ratios 1:8:16, as expected for a molecule containing two boron atoms (^{10}B:^{11}B = 1:4)) are always found at *m/e* 326, 327, and 328 respectively, with intensities lying between 27 and 88%. The spectra further show a gradual breakdown of the molecules. As the starting acetylene becomes more asymmetrical, the differences in intensities of the parent peaks of the two DBCH isomers grow larger. The intensity of the parent peak of [MeBC$_4$*n*-Bu$_4$BMe] is 28%; the intensities of the parent peaks of the two isomers of [MeBC$_4$*n*-Pr$_2$*n*-Pent$_2$BMe] are 52% and 60%, respectively, those of [MeBC$_4$Et$_2$*n*-Hex$_2$BMe] 42 and 88%, respectively. In our opinion, the parent peak with the highest intensity originates from the least sterically hindered isomer.

There is a characteristic difference between the mass spectra of the 1,4-DBCH's on the one hand and the mass spectra of 1,4-disilacyclohexa-2,5-dienes and 1,4-digermacyclohexa-2,5-dienes[32] (synthesized by reaction of silylenes and germylenes, respectively, with diphenylacetylene) on the other. In the latter a main fragmentation pattern involves

formation of the starting acetylene. In none of the DBCH mass spectra any indication for this mechanism was found. This is probably due to the considerable π-interaction over the hetero atom in the DBCH's, which is absent in the corresponding silicon and germanium compounds.

The mass spectrum of 1-methyl-2,3-di-t-butylborirene (XIII) is characterized by the following fragmentation scheme, in which isotope peaks are omitted. $164 = M^+$ (64%), $149 = [M-CH_3]^+$ (63%), $107 = [M-C_4H_9]^+$ (100%), $93 = [149-C_4H_8]^+$ (22%), $77 = [93-CH_4]^+$ (7%), $65 = [107-C_3H_6]^+$ (75%), $51 = [93-C_3H_6]^+$ (17%), $41 = [(CH_3)_2B]^+$ (52%) (fragmentation of the ring). It is suggestive for the stability of (XIII) that throughout the fragmentation of the molecule the borirene-ring stays intact.

The main fragmentation scheme of 1,3-dimethyl-2,4-di-t-butyl-1,3-diboretene (XVb) is as follows (isotope peaks omitted): $190 = M^+$ (4%), $175 = [M-CH_3]^+$ (77%), $148 = [M-C_3H_6]^+$ (11%), $133 = [M-C_4H_9]^+$ and/or $[148-CH_3]^+$ (84%), $119 = [175-C_4H_8]^+$ (39%), $117 = [133-CH_4]^+$ (47%), $105 = [133-C_2H_4]^+$ (13%), $95 = [t-BuCBMe]^+$ (34%), $91 = [117-BCH_3]^+$ (23%), $77 = [119-C_3H_6]^+$ (12%), $65 = [91-C_2H_2]^+$ (51%), $41 = [(CH_3)_2B]^+$ (100%).

Preliminary NMR data for borirene (XIII) and diboretene (XVb) are given in Ref. 30 The ^{1}H NMR data of the DBCH derivatives described in this publication proved these compounds to be planar.

In the reactions of almost all dialkylacetylenes with the system $2C_8K/MeBBr_2$ hexaalkylbenzenes were formed: with di-n-butylacetylene hexa-n-butylbenzene, with n-propyl-n-pentylacetylene tri-n-propyl-tri-n-pentylbenzene, and with ethyl-n-hexylacetylene triethyl-tri-n-hexylbenzene. However, in each of the latter two cases, only one isomer could be detected by GC/MS.

The formation of hexaalkylbenzenes might be explained by the reaction of a molecule of borirene (XVIII) with one molecule of acetylene, leading to the formation of a borole (XIX). Another molecule of acetylene might undergo a Diels–Alder reaction with the borole, leading to the formation of a 7-borabicyclo[2.2.1]heptadiene (XX) which, via a [1,3] suprafacial sigmatropic rearrangement, would give a 7-borabicyclo[4.1.0]heptadiene (XXI). This compound, on the one hand might yield a borepin (XXII) via a disrotatory ring opening, or, on the other hand, might eliminate a borylene to form a benzene derivative (XXIII); see Fig. 2.

Recently, Eisch et al. reported[26] the photochemical reaction of diphenylacetylene with a solution assumed to contain the pyridine complex of
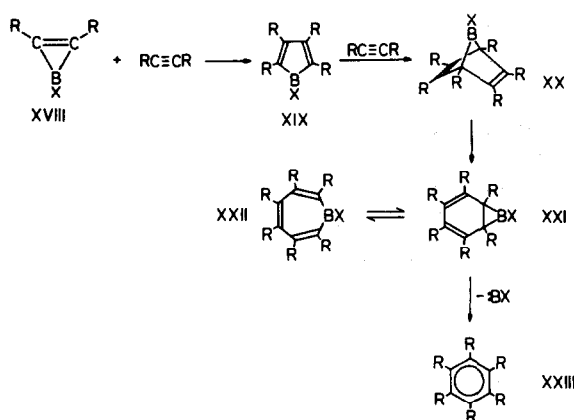

Fig. 2.

triphenylborirene, to produce the pyridine complex of pentaphenylborole. The formation of a benzene derivative from a borole via the Diels–Alder addition of an acetylene has been suggested by Grisdale and Williams.[33] The synthesis of heptaphenylborepin from pentaphenylborole and diphenylacetylene has been described by Eisch and Galle.[34] Our own researches have shown[35,36] that 1-methylborepin eliminates methylborylene in a symmetry-allowed reaction to yield benzene, probably via a 7-borabicyclo[4.1.0]heptadiene.

The apparent occurrence of only one "benzene isomer" in the case of asymmetrical acetylenes might be explained on grounds of steric hindrance. The same argument applies to the fact that in the reactions of di-t-butylacetylene absolutely no hexa-t-butylbenzene was found.

It should be noted that we never found any trace of boroles. This can be explained by assuming that the Diels–Alder reaction of an acetylene with a borole is much faster than the cycloaddition reaction of an acetylene with a borirene, an assumption that is borne out by orbital-symmetry arguments:[37] the latter reaction is forbidden in the ground state.

DISCUSSION

In the foregoing it has been shown that C_{10} dialkylacetylenes are suitable substrates for the synthesis of 1,4-diboracyclohexa-2,5-diene (DBCH) derivatives, upon reaction with the system $2C_8K/MeBBr_2$. When the extremely sterically crowded di-t-butylacetylene was used as a substrate, it proved possible to obtain the corresponding borirene and diboretene derivative. Therefore it is assumed that the formation of DBCH's proceeds via dimerization of initially formed borirenes.

When dimethylacetylene (2-butyne) is reacted with C_8K and $MeBBr_2$ in benzene, the first reaction to take place is fast haloboration (as was estab-

lished by ^{1}H NMR). Gradually, the haloboration product is converted by the C_8K, however, not in hexamethyl-DBCH, but in a compound the ^{1}H NMR spectrum of which showed two MeB signals (of equal intensity) and two MeC resonances (of equal intensity). The intensity ratio of the MeB and the MeC peaks was 1:2. This provided strong evidence for a nido-carborane structure in which the boron atoms are inequivalent. The ^{1}H NMR data of this compound matched those given in the literature for hexa- methyl-2,3,4,5-tetracarbahexaborane(6).[41]

In the same reaction, GC/MS investigation showed that, in small amounts, two species were present the fragmentation and isotope pattern of which suggested the compositions $[C_2Me_2]_2[MeB]_4$ and $[C_2Me_2]_3[MeB]_4$. These probably carborane-like structures proved to be resistant to acetolysis with glacial acetic acid.

Further, recent experiments have shown that, when diethylacetylene (3-hexyne) is reacted with the system $2C_8K/MeBBr_2$ at room temperature, the molecule $[MeBC_4Et_4BMe]$ with nido-carborane structure is formed. When the same reaction is carried out at reflux temperature, both the carborane and the DBCH structure are formed.

In our opinion the formation of the 2,3,4,5-tetracarbahexaboranes(6) takes place via reaction of C_8K with the haloboration product.

Concerning the formation of the planar DBCH's, it should be noted that, in the reactions of the system $2C_8K/MeBBr_2$ with decynes, upon longer reaction times, when the potassium content of the surface of the graphite–potassium has become low, small amounts of the corresponding carboranes are formed.

At the moment, we are unable to discern between the following two possibilities.

(a) The formation of DBCH and carborane takes place via two independent reactions, the former involving the boron analogue of a carbenoid reaction with the acetylene, leading to the formation of a borirene which dimerizes, the latter involving an attack of the graphite–potassium on the haloboration product.

(b) Both borirene (and thus DBCH) and carborane are formed via the haloboration product. Whether DBCH or carborane is formed is determined by the bulkiness of the acetylene and the potassium content of the surface of the graphite–potassium.

EXPERIMENTAL

All experiments were carried out in an atmosphere of dry, oxygen-free nitrogen. Solvents were purified and stored under nitrogen. Liquids were handled with syringes.

^{1}H NMR spectra were recorded using Varian EM 390 and HA-100 spectrometers. ^{13}C NMR spectra were recorded on a Bruker WM 250 spectrometer by Dr. F. J. J. de Kanter at the Chemical Laboratory of the Free University at Amsterdam. GC/MS investigations were carried out on a Finnigan 3100 D Mass Spectrometer with 6110 Data System and Finnigan 9500 Gas Chromatograph by Miss E. Ch. Th. Gevers, Mrs. G. G. Versluis-de Haan, and Mrs. C. M. Bijlsma-Kreuger at the Institute for Organic Chemistry TNO at Utrecht, and on a Kratos MS 80 Mass Spectrometer with Data General Nova 3 Data System and Carlo Elba/Kratos Gas Chromatograph by Mrs. A. van der Kerk-van Hoof at the Laboratory for Analytical Chemistry of the State University at Utrecht.

Tetramethyltin was kindly provided by the Institute for Organic Chemistry TNO at Utrecht. . MeBBr$_2$ was synthesized from Me$_4$Sn and BBr$_3$.[38,39] C_8K was synthesized according to a literature procedure.[40] Concerning the latter, it should be noted that the graphite should be very thoroughly dried prior to the synthesis of C_8K, to prevent the formation of oxygen-containing products in the subsequent syntheses.

Reactions of 5-decyne, 4-decyne and 3-decyne with the system $2C_8K/MeBBr_2$

These reactions were all carried out in the same fashion. In a typical run, 24.74 g (183 mmole) of C_8K were suspended in 100 cm^3 of benzene and 10.78 g (78 mmole) of 5-decyne were added. The mixture was heated to reflux and 14.67 g (79 mmole) of MeBBr$_2$, diluted with 20 cm^3 of benzene, were added dropwise over a period of ca. 1 hr. The reaction was followed with ^{1}H NMR and the suspension turned black. The reaction mixture was refluxed for 20 hr and next stirred at room temperature for 3 more days. After that period all solid material was removed by filtration (or centrifugation). A dark-brown liquid was obtained from which all volatile components were removed in vacuo. The residue was subjected to fractional vacuum distillation. The fraction boiling at 60–65°/10^{-6} Torr was, according to GC/MS, pure 1,4-dimethyl-2,3,5,6-tetra-n-butyl-1,4-diboracyclohexa-2,5-diene. This compound is a viscous yellow liquid, very air- and moisture sensitive, and thermally somewhat unstable. The same reaction, carried out in cyclohexane, yielded the same results.

Reaction of 2-butyne with the system $2C_8K/MeBBr_2$

In 100 cm^3 of benzene were suspended 20.56 g (152 mmole) of C_8K; 4.11 g (76 mmole) of 2-butyne

were added to this mixture. Next, 14.12 g (76 mmole) of MeBBr$_2$ diluted with 20 cm^3 of benzene were added dropwise. The ensuing reaction was slightly exothermic; the graphite-potassium slowly turned black. The mixture was stirred at room temperature for 6 days. After this period, all solid material was removed by centrifugation. The supernatant was investigated by GC/MS. The carborane was obtained in a pure state by fractionated vacuum distillation (b.p. 55–56°/4.5 Torr). It is a pale yellow liquid, extremely sensitive towards air and water.

The same product is obtained when 2-butyne is reacted first with one equivalent of MeBBr$_2$ (in benzene), and the reaction product is treated subsequently with two equivalents of C$_8$K.

In the mass spectrum of [MeBC$_4$Me$_4$BMe] the base peak is the parent peak (m/e 160). The ratio of the peaks at m/e 158, 159 and 160 is 1:8:16. Further prominent peaks occur at m/e 145 ([M–CH$_3$]$^+$, 69%), m/e 65 ([C$_2$BMe$_2$]$^+$, 43%), and at m/e ([Me$_2$B]$^+$, 50%).

Reaction of di-t-butylacetylene with the system 2C$_8$K/MeBBr$_2$; formation of 1-methyl-2,3-di-t-butylborirene (XIII) and of 1,3-dimethyl-2,4-di-t-butyl-1,3-diboretene (XVb)

Two portions of ca. 150 mmole of C$_8$K were each suspended in 100 cm^3 of benzene. To each half an equivalent (75 mmole) of di-t-butylacetylene were added. One of the mixtures was heated to reflux, and to both half an equivalent of MeBBr$_2$, diluted with 20 cm^3 of benzene, were added dropwise. Next, both mixtures were stirred for 3 days, one at reflux temperature, one at ambient temperature. The reactions were followed by ^{1}H NMR. When the reactions would not proceed any further, all solid material was removed by centrifugation. From the supernatants all volatile components were removed by freezing them *in vacuo* (10^{-1} Torr) into a trap cooled with liquid nitrogen. The liquids thus obtained appeared to contain air- and moisture-sensitive component(s). Most benzene was removed by careful distillation under atmospheric pressure over a Widmer column. The residues, colourless, extremely air- and moisture-sensitive liquids, contained, according to ^{1}H NMR, two t-butyl components, apart from di-t-butylacetylene. The residues of both distillations and the residues obtained after removal of all volatile components were investigated by GC/MS. The latter contained no identifiable compounds.

Acetolysis of reaction mixtures

Prior to acetolysis all solid material was removed

by filtration or centrifugation. Next, an excess of glacial acetic acid was added and the mixture was refluxed for 1 hr.

Residues were diluted with benzene before the acetic acid was added.

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