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FORMATION AND SOME PROPERTIES OF THE AROMATIC COMPOUND 1-METHYLBOREPIN

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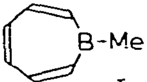
Summary

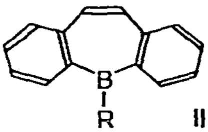
The aromatic compounds 1-methylborepin (I) and 1-methyl-3,6-dideuteroborepin (XXII) are formed in the reactions between methylboron dibromide and the products of the hydrostannation of a 1/1 *cis/trans* mixture of 1,5-hexadiyn-3-ene (XIV) with diethylbromotin hydride and diethylbromotin deuteride, respectively. I and XXII are thermally unstable, yielding benzene and 1,4-dideuterobenzene, respectively, on decomposition.

We describe below the formation and identification of a non-annelated borepin, viz. 1-methylborepin (I).

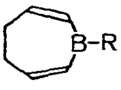

I

The possibility that borepins could be aromatic was recognized as early as 1958 by Vol'pin [1]. The first compound formally containing the borepin unit, dibenzoborepin (IIa, b), was synthesized in 1960 by Van Tamelen and Brieger [2,3], but Dewar has pointed out that the degree of aromatic stabilization of the borepin unit in IIa and IIb must be small [4].

Attempts to synthesize non-annelated borepins, however, were unsuccessful. Sheehan [5] synthesized the dihydro derivatives IIIa—IIId, but could not introduce the third double bond.


II

a $R = OCH_2CH_2NH_2$
b $R = H$


III

a $R = Ph$
b $R = OH$
c $R = Cl$
d $R = OCH_2CH_2NH_2$

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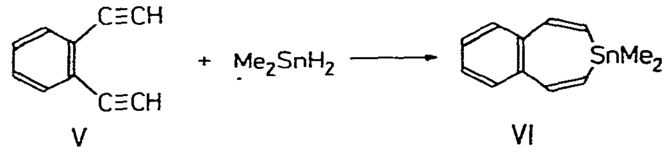
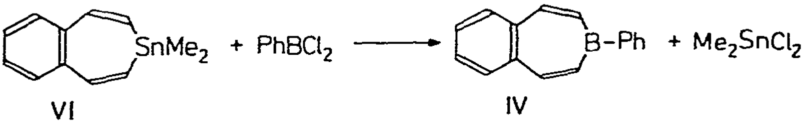
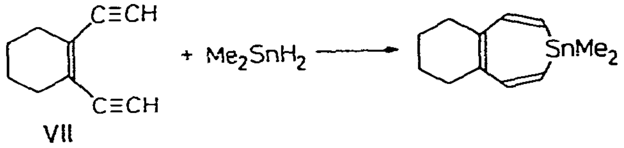
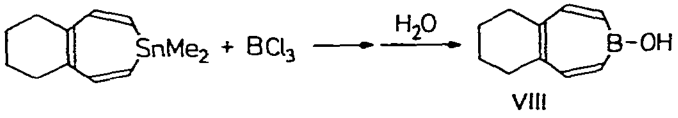
In 1967 the benzo derivative 3-phenyl-3-benzoborepin (IV) was synthesized by Leusink et al. [6]. Two steps were crucial in this synthesis, first, hydrostannation of 1,2-diethynylbenzene (V) with dimethyltin dihydride, to yield the benzostannepin VI, and second, the replacement of the tin atom in VI by boron:



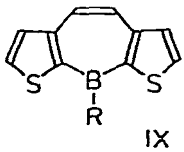


In 1971 Halpern [7,8] reported the addition of dimethyltin dihydride to 1,2-diethynylcyclohexene (VII). Upon replacement of tin by boron and subsequent hydrolysis the cyclohexenoborepin derivative VIII was obtained. The ^{1}H NMR data obtained by Halpern strongly indicated aromaticity for VIII.



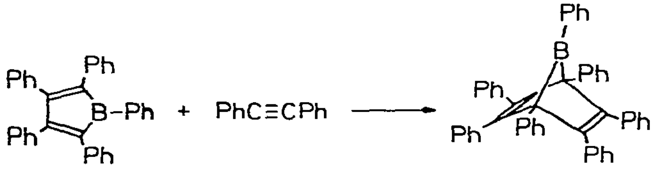


Jeffries and Gronowitz [9] in 1973 synthesized the borepino[3,2b;6,7b′]-dithiophenes IXa—IXd. They presented ^{1}H and ^{11}B NMR and UV spectral data

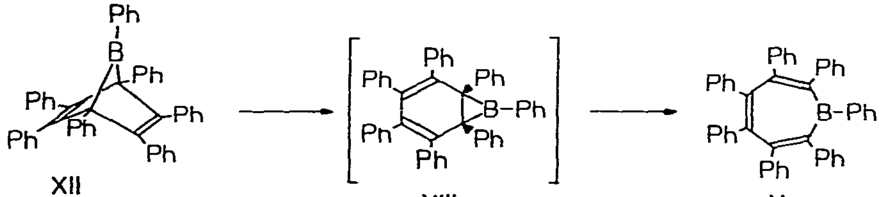


a $R = OCH_2CH_2NH_2$
b $R = OH$
c $R = C_{10}H_6BS_2$
d $R = Me$

in evidence for the aromatic character of the compounds. In 1975 Eisch and Galle [10] reported an elegant synthesis of heptaphenylborepin (X) and of 1-phenyl-2,3,4,5,6,7-hexa-*p*-tolylborepin. A Diels-Alder reaction was carried out between pentaphenylborole (XI) [11] and diphenylacetylene, yielding heptaphenyl-7-borabicyclo[2.2.1]heptadiene (XII); next a [1,3] suprafacial sigmatropic rearrangement of XII gave the intermediate heptaphenyl-7-borabicyclo[4.1.0]heptadiene XIII, this rearrangement being followed by a disrotatory ring opening yielding heptaphenylborepin (X):



XI XII

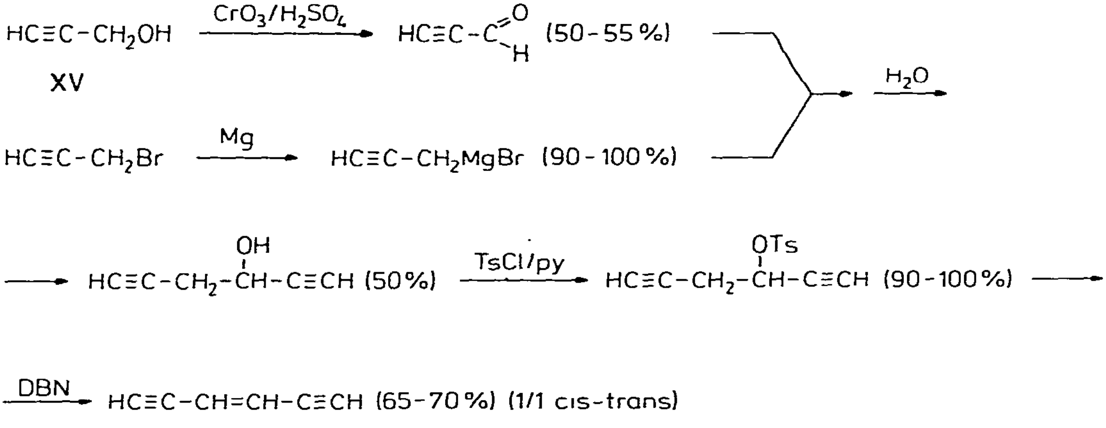


XII XIII X

In their paper Eisch and Galle suggested the existence of an equilibrium between the valence isomers X and XIII. On the basis of UV and IR spectroscopic data and changes therein upon complexation with pyridine or gaseous ammonia, they concluded that heptaphenylborepin is aromatic.

Further, research has been done in the field of highly annelated borepins, such as bora-anthracene systems [12,13], but in these systems the aromatic properties of the borepin nucleus may be obscured or even destroyed by the benzene rings.

We thought that a suitable way of synthesizing a non-annelated borepin might be the tin route developed by Leusink et al. [6] and followed by Halpern [7], but with *cis*-1,5-hexadiyn-3-ene (XIV) as the starting compound. The 1,5-hexadiyn-3-ene was obtained according to the following scheme (the average yields for the several reactions are indicated in parentheses):



$$HC\equiv C-CH_2OH \xrightarrow{CrO_3/H_2SO_4} HC\equiv C-C\overset{O}{\underset{H}{\diagdown}}\ (50-55\%)$$

XV

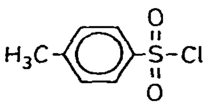
$$HC\equiv C-CH_2Br \xrightarrow{Mg} HC\equiv C-CH_2MgBr\ (90-100\%)$$

$$\xrightarrow{H_2O}\ \longrightarrow HC\equiv C-CH_2-\overset{OH}{\overset{|}{C}}H-C\equiv CH\ (50\%) \xrightarrow{TsCl/py} HC\equiv C-CH_2-\overset{OTs}{\overset{|}{C}}H-C\equiv CH\ (90-100\%) \longrightarrow$$

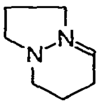
$$\xrightarrow{DBN} HC\equiv C-CH=CH-C\equiv CH\ (65-70\%)\ (1/1\ cis-trans)$$

XIV

TsCl =

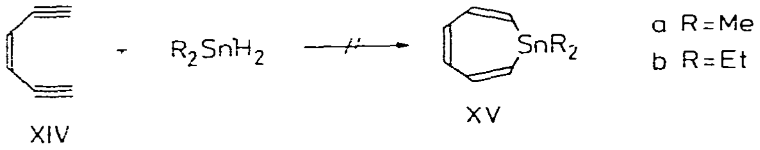


DBN =



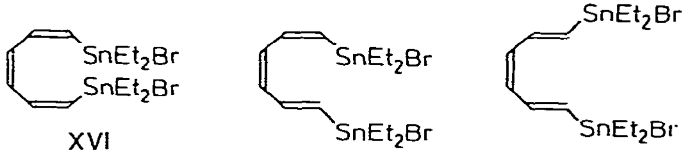
diazabicyclo[4 3 0]non-5-ene

Starting from propargyl alcohol (XV), an overall yield of 15—19% of an equimolar *cis/trans* mixture of 1,5-hexadiyn-3-ene was obtained. This 1/1 *cis/trans* mixture of 1,5-hexadiyn-3-ene did not, however, react with organotin hydrides of the types R_2SnH_2 (R = Me, Et) and R_3SnH (R = Ph). At the temperatures required for the addition of these organotin hydrides to carbon—carbon triple bonds (50—60° C), polymerization of XIV was so fast that no hydrostannation

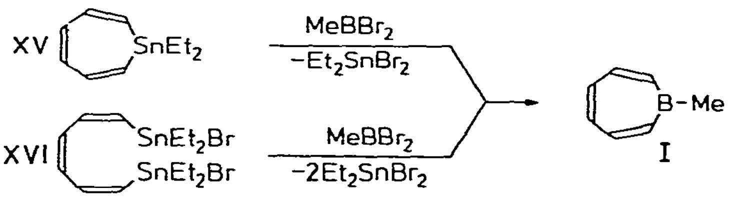


took place. Under these conditions no trace of benzene was formed from XIV, and this is of significance in view of observations reported below.

To circumvent the unreactivity of XIV towards common organotin hydrides, the extremely reactive organohalotin hydride Et_2BrSnH was employed. Not only did XIV and Et_2BrSnH react, but the Et_2BrSnH inhibited the polymerization of XIV. The ^1H NMR and IR spectra of the product mixture showed that hydrostannation had taken place, but all attempts to isolate the stannepin XVb were in vain. The hydrostannation mechanism likely in the case of an acetylenic compound like XIV is the radical β mechanism [14a—c], and several isomeric products are to be expected from such a reaction of the *cis* isomer of XIV with Et_2BrSnH:



In addition, of course, products formed by hydrostannation of the *trans* isomer will also be formed. Only the all-*cis* addition product XVI can eventually lead to the formation of a borepin. As a consequence, the overall yield of the latter would be very low. The stannepin XVb could not be obtained from the reaction mixture. It was thought, however, that not only the stannepin XVb but also the all-*cis* product XVI might products 1-methylborepin (I) upon treatment with methylboron dibromide:



It should be noted that the replacement of tin by boron is most likely to occur with retention of configuration [15].

A large-scale reaction (0.85 mol) between a 1/1 *cis/trans* mixture of 1,5-hexadiyn-3-ene (XIV) and Et_2BrSnH (undertaken in view of the expected low overall yield of 1-methylborepin (I) resulted in a violent explosion. Conse-

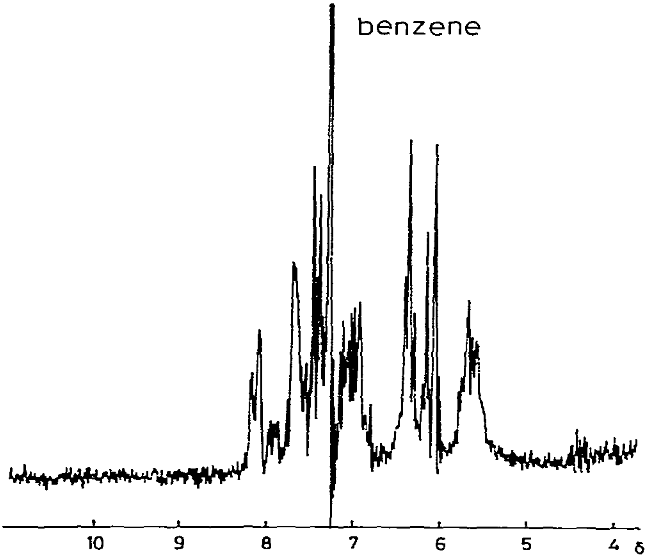
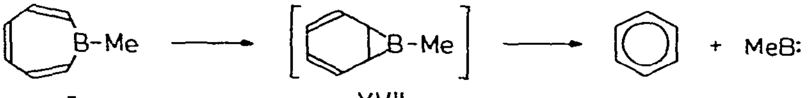


Fig. 1. ^{1}H NMR spectrum of the contents of the cold trap after the reaction of $MeBBr_2$ with the products of the addition reaction between Et_2BrSnH and 1,5-hexadiyn-3-ene (in n-pentane).

quently, later experiments were carried out on a much smaller scale.

Eventually, the formation of I was achieved by adding $MeBBr_2$ to the mixture of products of the addition reaction between XIV and Et_2BrSnH in n-pentane. The resulting reaction was exothermic and fast; after its completion all volatile components were drawn off into a cold trap. Since the boiling point of I was expected to be rather low, the ^{1}H NMR spectra were recorded of the contents of the cold trap. One such spectrum is shown in Fig. 1. A conspicuous feature in these spectra is a benzene peak at δ 7.28 ppm. It must be emphasized that at no stage in the overall reaction sequence aiming at 1-methylborepin, had benzene been used. If, however, I had been formed, it could have given benzene by the following sequence:



I XVII

1-Methylborepin is expected to have an AA′BB′CC′ proton NMR spectrum. The spectrum of the boranorcaradiene derivative XVII should be of the same type, though the chemical shifts of the individual ring protons in XVII should differ vastly from those in I. The set of signals present in the ^{1}H NMR spectrum of the contents of the cold trap ranges from δ 8.3 to δ 5.4 ppm (see Fig. 1), which is too large to allow the assignment of this set to one single species. In our opinion, the signals between δ 8.3 and δ 6.9 ppm, falling in the aromatic part of the spectrum, originate from 1-methylborepin (I). The signals between δ 6.5 and δ 5.4 ppm then might indicate the presence of 7-methyl-7-borabicyclo[4.1.0]heptadiene (XVII), in which compound the double bonds have olefinic character, in contrast to those in I. The formation of an intermediate

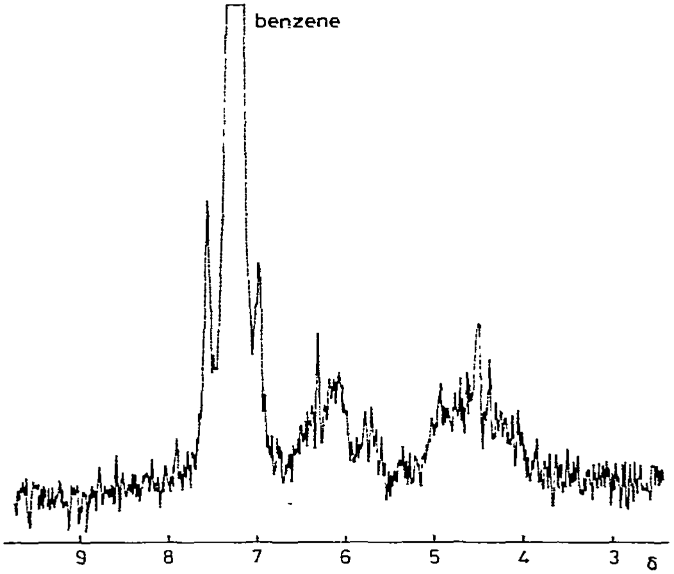


Fig. 2. ^{1}H NMR spectrum of the dimethylamine complex of the contents of the cold trap (see Fig. 1) (in DMSO-d_6).

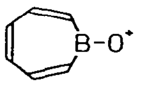
boranorcaradiene derivative, as suggested by Eisch [10], is analogous to the formation of benzene oxide from oxepin [16,17]. No high-field absorptions could be observed in our spectra, since they were recorded in n-pentane.

In their work on 3-phenyl-3-benzoborepin (IV), Leusink et al. [6] had observed that the ^{1}H NMR and UV spectra of IV change significantly when the boron atom in IV is complexed by dimethylamine, a reaction which is easily reversible. The observed change can be understood in terms of loss of aromaticity of the borepin ring. Consequently, part of the contents of the cold trap were treated with dimethylamine. A yellowish white precipitate was formed, which after thorough removal of the solvent was dissolved in DMSO-d_6. A ^{1}H NMR spectrum was recorded after 90 minutes and is shown in Fig. 2. Not only had the spectrum changed completely, compared with that of 1-methylborepin (Fig. 1), but again the presence of benzene is evident. It should be noted that the noise level in the spectrum of the complex is high due to the low concentration of the sample.

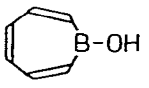
Further ^{1}H NMR investigations showed the contents of the cold trap also to be thermally unstable; again benzene was formed, though more slowly than in the DMSO-d_6 solution of the dimethylamine complex. It should be mentioned that formation of benzene (in small quantity) had already been observed in the addition of Et_2BrSnH to XIV (in the polymerization of XIV no benzene is formed). Thus 1-methylborepin, its dimethylamine complex and the organotin intermediate(s) all appeared to be thermally unstable. In the following paper [18] this topic is considered from an orbital-symmetry point of view.

To obtain further information GC-MS was performed on the contents of the cold trap. At first the GC-MS results were somewhat confusing, since mass peaks were observed which could not immediately be related to the presence of 1-methylborepin (I), the parent peaks of which should occur at *m/e* 104 and

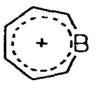
103 (with relative intensities 4 : 1 due to the natural abundance ratio of the boron isotopes: $^{11}B : ^{10}B = 80.22 : 19.78$). Interpretation was possible on the reasonable assumption that all the I had reacted with the column material to form demethylated and oxygen-containing species. In the mass spectrum the base peak was found at *m/e* 105, while the intensity of the peak at *m/e* 104 was 23% of that of the base peak. This is indicative of fragment XVIII. The presence of fragment XVIII is substantiated by the presence of the parent peak of XIX at *m/e* 106. The isotope peak of the latter then should contribute to the peak at *m/e* 105, which indeed is somewhat high when compared with its isotope peak at *m/e* 104 (in the formulae drawn above, the numbers in parentheses represent the relative intensities). The 1-hydroxyborepin (XIX) is thought to have been formed from I by interaction with the column material; it is very improbable that XIX was generated as a direct result of the reaction of the organotin hydride addition products with $MeBBr_2$. Confirmatory evidence for the presence of a borepin system is provided by the appearance of the boratropylium ion XX and of the boracyclopentadienylium ion XXI. The presence of XX and XXI in mass spectra of phenylorganoboranes has been reported before [19]. Conspicuously present also were the tropylium ion ($C_7H_7^+$, *m/e* 91 (98)) and the cyclopentadienylium ion ($C_5H_5^+$, *m/e* 65 (22)), probably formed



m/e 105 (100)
m/e 104 (23)
XVIII



m/e 106 (54)
XIX



m/e 89 (34)
m/e 88 (85)
XX

m/e 63 (19)
m/e 62 (5)
XXI

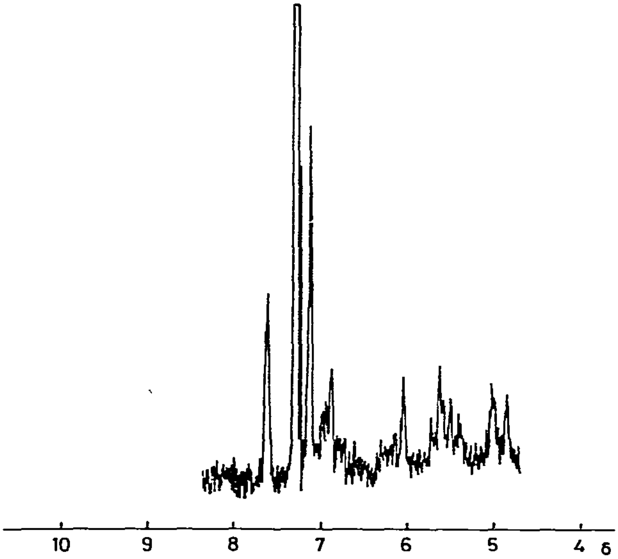
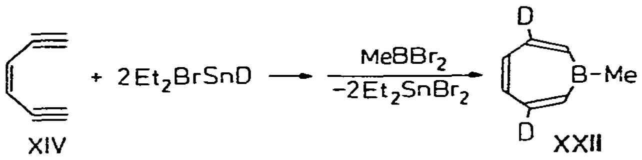


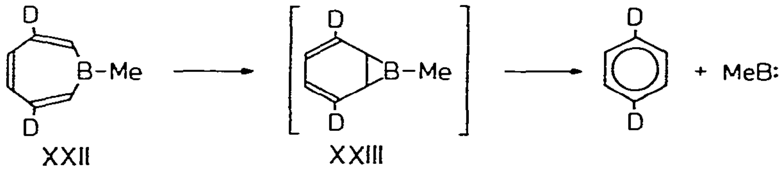
Fig. 3. ^1H NMR spectrum of the contents of the cold trap after the reaction of $MeBBr_2$ with the products of the addition reaction between Et_2BrSnD and 1,5-hexadiyn-3-ene (in CCl_4).

via electron impact-induced rearrangements.

In order to confirm the evidence obtained so far for the formation of 1-methylborepin, it was decided to carry out the reaction of XIV with diethylbromotin deuteride, Et_2BrSnD. It was envisaged that eventually 1-methyl-3,6-dideuteroborepin (XXII) would be formed (among other products).



The mixture obtained upon reaction of XIV with Et_2BrSnD yielded a ^1H NMR spectrum in which the olefinic signals, though still complicated, were much simpler than those in the spectrum of the adducts of XIV and Et_2BrSnH. Subsequently, $MeBBr_2$ was brought into reaction with the products of the addition reaction and all the volatile components were drawn off into a cold trap. As expected, the ^1H NMR spectra (one of which is shown in Fig. 3) proved to be much simpler than those of I. Again there was evidence for the occurrence of a boranorcaradiene derivative, in this case 7-methyl-2,5-dideutero-7-borabicyclo[4.1.0]heptadiene (XXIII). A further product, 1,4-dideuterobenzene, was also expected as a consequence of the following decomposition:



In the ^1H NMR spectra a signal was present at the chemical shift for benzene. On closer inspection at 1 ppm sweep width the signal proved to have a multiplet structure identical to that given by an authentic sample of 1,4-dideuterobenzene [20].

In summary, it seems justifiable to conclude that 1-methylborepin (I) and 1-methyl-3,6-dideuteroborepin (XXII) were formed and identified. However, the route used for their synthesis seems to be unsatisfactory for the production of larger amounts of these interesting compounds, as the yields are extremely low.

Experimental

General remarks

All reactions were carried out under dry nitrogen. Solvents were purified by distillation from calcium hydride. Transfers involving solutions of air- or moisture-sensitive compounds were effected with syringes.

^1H NMR spectra were recorded on a Varian EM 390 spectrometer. GC-MS investigations were carried out on a Finnigan 3100 D Mass Spectrometer with 6110 Data System and Finnigan 9500 Gas Chromatograph, using a 3% MePhSil. Fluid column (1.4 m glass OD 2 mm).

Synthesis of starting materials

3-Tosyl-1,5-hexadiyn was prepared from propargyl aldehyde [21] in a two-step synthesis using published procedures [22—25]. Diethyltin dichloride and diethyltin dibromide were synthesized from tetraethyltin and $SnCl_4$ and $SnBr_4$, respectively [26,27]. $SnBr_4$ was prepared by a published method [28,29]. Diethyltin dihydride was prepared by lithium aluminium hydride reduction of diethyltin dichloride [30,31]; diethyltin dideuteride was synthesized analogously by reduction of Et_2SnCl_2 with $LiAlD_4$ and hydrolysis with D_2O. Methylboron dibromide was synthesized from tetramethyltin and BBr_3 by a literature procedure [32].

Synthesis of 1,5-hexadiyn-3-ene (XIV)

Literature procedures [24,25] for the synthesis of 1,5-hexadiyn-3-ene were abandoned because the yields were too low (10—15%). Better yields (up to 75%) were obtained using the following method. A two-necked round-bottomed flask was charged with 70 g (0.28 mol) of 3-tosyl-1,5-hexadiyn. The flask was equipped with a pressure-equalizing funnel charged with 35 g (0.28 mol) of diazabicyclo[4.3.0]non-5-ene (DBN); the other neck of the flask was connected to a cold trap (cooled with liquid nitrogen). The system was evacuated and a safety shield placed in front of it. The tosylate was cautiously melted with an open flame and the DBN was added dropwise, with magnetic stirring. This way, the 1,5-hexadiyn-3-ene was drawn into the cold trap as soon as it was formed. The reaction was exothermic. After all DBN had been added, the mixture was heated cautiously to drive residual XIV into the cold trap. After the reaction vessel had cooled, nitrogen was admitted. The contents of the cold trap were thawed, diluted with 15 ml of ether, and washed six times with 1 *N* sulphuric acid (to remove any DBN) and once with water (both washing fluids were ice-cold to prevent polymerization of XIV). After washing, the ethereal solution was dried with $MgSO_4$ (on an ice-bath). The ethereal solution was stored at —80° C. The identity of XIV and the yield were established by ^1H NMR spectroscopy.

Addition of diethylbromotin hydride to 1,5-hexadiyn-3-ene

A mixture of 17.70 g (53 mmol) of Et_2SnBr_2 and 9.40 g (53 mmol) of Et_2SnH_2 was made at 0° C and was stirred for 30 minutes. Then 4.11 g (54 mmol) of 1,5-hexadiyn-3-ene, diluted with 15 ml of ether, were added. After five minutes stirring at 0° C the mixture was heated to reflux. The mixture of Et_2SnBr_2 and Et_2SnH_2 was colourless, though slightly cloudy; the 1,5-hexadiyn-3-ene had a light green colour (due to the presence of a slight amount of polymerization products). The reaction mixture, upon heating, changed colour from light green to orange-brown. After 16 hours refluxing no acetylenic proton signals could be observed in the ^1H NMR spectrum, and instead broad, complicated olefinic signals were visible. An infrared spectrum confirmed that all the acetylene had been converted. All the volatile components were removed in vacuo (at room temperature) to leave a red-brown viscous liquid with some white solid.

Formation of 1-methylborepin (I)

The residue obtained as described above was diluted with 35 ml of n-pentane. The mixture was cooled to 0°C and 9.70 g (52 mmol) of $MeBBr_2$ were added with stirring during 90 minutes. A yellow precipitate was formed, and the solution turned intensely red-brown. The reaction was exothermic. After all the $MeBBr_2$ had been added, stirring was continued for 30 minutes. All the volatile components were then drawn into a cold trap and examined by ^1H NMR spectroscopy (Fig. 1).

Reaction between 1-methylborepin and dimethylamine

The reaction between 1-methylborepin and dimethylamine was carried out in a 5 mm NMR tube. Gaseous Me_2NH was led through a sample of the contents of the cold trap (by means of a Pasteur pipette drawn out to a capillary). A yellowish white precipitate was formed which did not dissolve on saturation of the n-pentane with Me_2NH. The solid material was separated by centrifugation, all the n-pentane was removed, the solid material was dried by evacuation to remove all the benzene, and DMSO-d_6 was added. The precipitate dissolved and the ^1H NMR spectrum was recorded (Fig. 2).

Addition of diethylbromotin deuteride to 1,5-hexadiyn-3-ene

This reaction was carried out as described for the addition of diethylbromotin hydride.

Formation of 1-methyl-3,6-dideuteroborepin (XXII)

This reaction was carried out as described for I (the quantities used were 2.68 g (35 mmol) of 1,5-hexadiyn-3-ene, 11.86 g (35 mmol) of Et_2SnBr_2, and 6.37 g (35 mmol) of Et_2SnD_2) with the following modifications. After removal (in vacuo) of all volatile components from the mixture obtained from the hydrostannation, the residue was diluted with liquid paraffin. A mixture of 6.54 g (35 mmol) of $MeBBr_2$ and liquid paraffin was added. A red-brown solution and a yellow precipitate were formed. All volatile components were drawn into a cold trap. The contents of the cold trap were diluted with CCl_4 and ^1H NMR spectra were recorded (Fig. 3).

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