RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

March 1968

U. D. C. 546.27 : 547.244

Organoelementary Derivatives of Barenes (Carboranes-10)

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I. INTRODUCTION

One of the most surprising peculiarities of the icosahedral system of barene (carborane-10) and neobarene† is the unusual valency state of the two carbon atoms, each of which is bound simultaneously to six other atoms (Fig. 1).

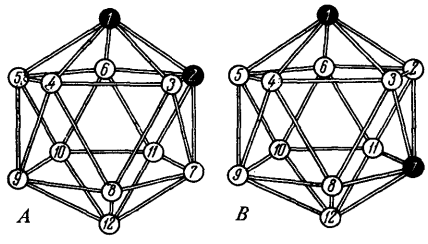


Figure 1. Structure of: *A*) barene; *B*) neobarene.

† The American name for barene is 1,2-dicarbaclovododecaborane-12, carborane-10, or ortho-carborane; neobarene is termed by them neocarborane or meta-carborane. For further details on the nomenclature of the barenes see Ref.1.

This fact, coupled with the strong electron-acceptor properties of the barene cage and the steric hindrance which it creates, makes the study of *C*-functional derivatives of barene extremely interesting. From the point of view of organoelementary chemistry the greatest interest attaches to derivatives containing a direct bond between the element and a cage carbon atom. The investigation of such compounds can obviously give valuable information on the nature and properties of the element–carbon bond in general.

The first papers reporting the discovery of barenes appeared at the end of 1963.[2-5]. A general method for synthesising them consists in the reaction of decaborane with acetylenes in the presence of Lewis bases:

$$B_{10}H_{14} + RC{\equiv}CR' \xrightarrow{L} RC\!-\!CR' + 2H_2$$

(the product is bonded to $B_{10}H_{10}$)

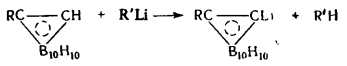
The chemical structure of barene, established theoretically by Lipscomb[6], was confirmed by X-ray[7-10] and electron[11] diffraction, although the first X-ray results subsequently proved to be erroneous[2]. The ten boron atoms and two carbon atoms of barene form an almost regular icosahedron (with interatomic distances C–C = 1.64–1.70 Å, B–C = 1.70–1.71 Å, and B–B = 1.70–1.79 Å), the C–C

bond length having no analogy throughout organic chemistry.

Barenes, in contrast to the original hydroboron, are stable towards oxidising agents, alcohols, strong acids, and bases, and possess phenomenal thermal stability. At 500°C barene isomerises into neobarene, in which the two carbon atoms are in the "meta" position relative to one another[12,13]. The chemical properties of barenes have recently been reviewed by Issleib et al.[14], and therefore we shall henceforward consider only those which are significant for the present paper. The most important of these properties is the "acidic" character of the C–H bonds, as a consequence of which the protons attached to the carbon atoms can be fairly easily replaced by alkali metals when the barenes are treated with the amides or lithium alkyls.

II. MAGNESIUM AND ALKALI-METAL DERIVATIVES; SYNTHESES BASED ON THEM

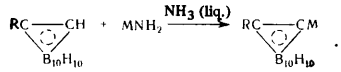
Organolithium derivatives of barenes, which are widely used for the synthesis of various barenyl compounds, are readily obtained by the action of butyl-lithium[15–17] or phenyl-lithium[16–18] both on barene itself and on monoalkyl- and monoaryl-barenes:



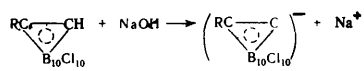
The reaction is usually accomplished by treating the barenes with a benzene solution of butyl-lithium at 60–80°C.[15]

To obtain the monolithium derivative of barene itself, the reaction must be conducted in ether at 0°C, and the solution of n-butyl-lithium or phenyl-lithium added to the barene in such a manner that excess of the latter is present throughout the reaction[16]. In contrast to this, the addition of an ethereal solution of barene to excess of n-butyl-lithium at 0–15°C results in a good yield of dilithiumbarene[16]. This derivative is obtained also by the action of excess of n-butyl-lithium in heptane or pentane on barene in tetrahydrofuran and of phenyl-lithium on barene in ether[17]. Neobarene undergoes methylation under similar conditions[12].

The sodium derivatives of barenes, the possibility of whose synthesis by the action of sodamide on the corresponding barenes was shown by Zakharkin et al.[19], are of great value for preparative purposes. This reaction was subsequently extended to the amides of other metals (lithium, potassium, calcium)[20,21]:

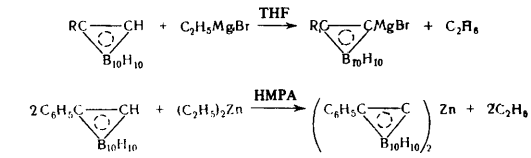


The ease of metallation of barenes by metal amides and lithium alkyls indicates the acidic character of the hydrogen atoms attached to the carbon atoms of the barene cage, this being due to the strong electron-acceptor action of the cage. Replacement by chlorine atoms of the hydrogen atoms attached to boron reinforces the electron-acceptor effect of the barene cage. The acidity of the decachlorobarenes has increased so much that they are now actual proton acids, which should dissolve in weak aqueous solutions of alkalis to give the corresponding sodium derivatives in the completely ionised state[22]:



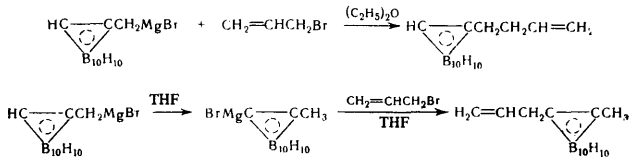
where R = H, C_6H_5.

In contrast to the reactions with lithium alkyls and metal amides, however, the hydrogen atoms attached to the carbon atoms of the barene cage are not replaced by a metal atom on treatment with organomagnesium and organozinc compounds in ethereal medium. The reaction goes only when complexing solvents are used. Thus ethylmagnesium bromide reacts smoothly with barene, methylbarene[17], and neobarene[23] in tetrahydrofuran (THF) medium, and diethylzinc reacts with phenylbarene in hexamethylphosphoramide (HMPA) medium[24]:

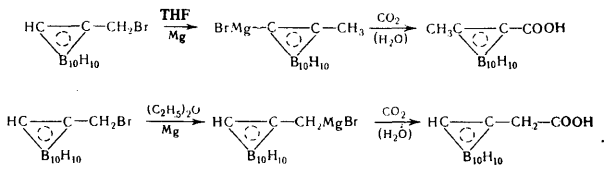


where R = H, CH_3.

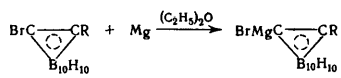
An interesting reaction was discovered by a group of American chemists[17] when preparing a Grignard reagent from bromomethylbarene. It was found that in tetrahydrofuran (unlike ether) the barenylmethylmagnesium bromide underwent isomerisation, and on treatment with allyl bromide gave 1-allyl-2-methylbarene instead of 4-barenylbut-1-ene:



The occurrence of such isomerisation was confirmed by Stanko[25], who showed that carboxylation in tetrahydrofuran of the Grignard reagent obtained from bromomethylbarene yielded methylbarenecarboxylic acid. When the reaction was conducted in ether, barenylacetic acid was formed:



Barenylmagnesium halides were obtained also directly from compounds containing a cage carbon–halogen bond:



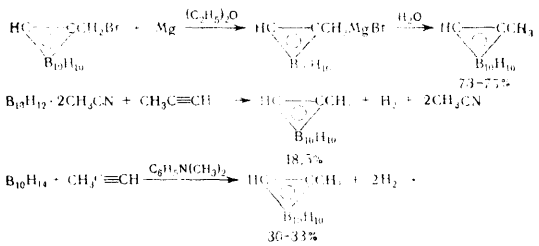
where R = n-C_3H_7, n-C_4H_9. However, these compounds did not react with aldehydes or ketones[16]‡.

The ease with which barenyl derivatives of elements in Groups I and II can be obtained has enabled a large number of diverse barenyl compounds to be synthesised on their basis.

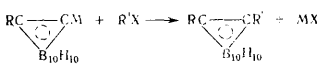
The carboxylation of barenylmethylmagnesium bromide mentioned above provides a more convenient method for preparing barenylacetic acid than synthesis from decaborane and ethyl but-3-ynoate[25]. Formation of methylbarene by the hydrolysis of barenylmethylmagnesium bromide occurs with a far better yield[16,26] than is obtained by the

‡ It has recently been reported[87] that analogous Grignard reagents, containing hydrogen, methyl, vinyl, and phenyl as substituents, react readily with aldehydes and ketones, as well as with alkyl halides[88].

reaction of propyne with decaborane in the presence of a Lewis base[27,28]:

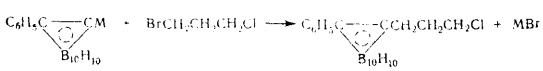


The alkylation of *C*-metal derivatives of barenes was investigated by several American chemists[12,16-18,29,30], and has subsequently been subjected to detailed study by Zakharkin and Kazantsev. They have synthesised a large number of alkyl and aryl derivatives of barene[20,21,31] and neobarene[32] on the basis of the reaction



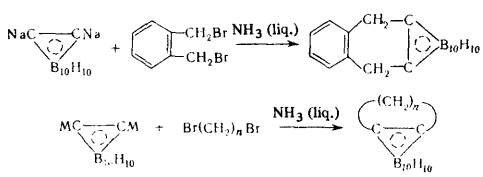
where M = Li, Na, K.

It is more convenient to work with sodium derivatives in liquid ammonia than with lithium derivatives in benzene or ether. Primary alkyl bromides and iodides, alkenyl bromides, $\alpha\omega$-dibromoalkanes (other than 1,2-dibromoethane), chloro-derivatives such as benzyl chloride, and dialkyl sulphates react smoothly. Primary alkyl chlorides react extremely slowly with metal derivatives of the barenes, and this permits the selective alkylation of the *C*-metal derivatives by $\alpha\omega$-bromochloroalkanes with the formation of α-barenyl-ω-chloroalkanes[31]:

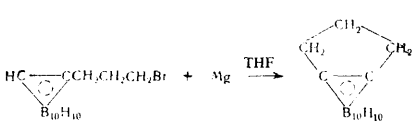


where M = Li, Na.

With secondary and tertiary alkyl bromides practically no alkyl derivatives are formed[31]. Barene derivatives containing two metal atoms react with certain $\alpha\omega$-dihalogeno-derivatives to give five- and six-membered carbocyclic compounds[31,33]:

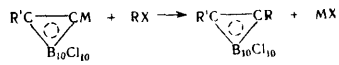


where M = Na, K and n = 3, 4. An analogous five-membered cyclic derivative is formed when an attempt is made to prepare a Grignard reagent from barenylpropyl bromide[34]:

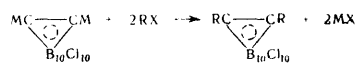


Such cyclisation is explained by metallation by the resulting Grignard reagent of another molecule of the halogenated barene followed by elimination of magnesium bromide.

C-Alkylation of *B*-decachlorobarene goes smoothly by the action of alkyl halides either on lithium salts of decachlorobarene in ethereal or toluene medium[35] or on the analogous sodium derivatives in alcoholic or aqueous-alcoholic medium[36]:



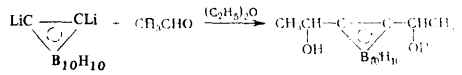
where M = Li, R = CH_3, C_2H_5, R′ = H, X = I;
or M = Na, R = CH_3, R′ = C_2H_5, X = I;
R = C_2H_5, R′ = H, X = I;
R = CH_2 : $CH.CH_2$, R′ = H, X = Br;
R = $C_6H_5.CH_2$, R′ = H, X = Cl;



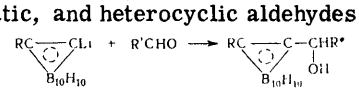
(M = Li, R = CH_3, C_2H_5, X = I or M = Na, R = CH_3, X = I).

The lithium derivatives of barene readily react with various aldehydes, from which alcohols can be obtained containing the hydroxyl in the α-position with respect to a carbon atom of the barene cage[20,21,37,38].

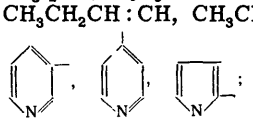
Heying et al.[16], who were the first to accomplish a reaction of this type, used dilithiumbarene, from which the corresponding diol was obtained by reaction with acetaldehyde:



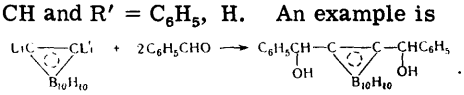
This reaction was subsequently extended to several aliphatic, aromatic, and heterocyclic aldehydes[37,38]:



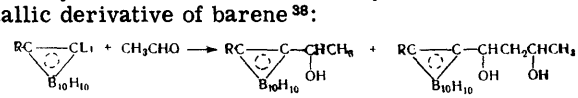
where R = CH_3, $(CH_3)_2CH$, C_6H_5 and R′ = C_6H_5; R = CH_3, C_6H_5 and R′ = H, $CH_3CH_2CH:CH$, $CH_3CH:CH$, *p*-$CH_3OC_6H_4$ *o*-ClC_6H_4,



R = $CH_2:CH$ and R′ = C_6H_5, H. An example is

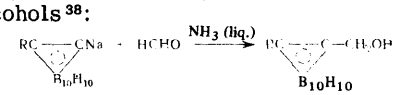


Reaction of lithiumbarenes with acetaldehyde may result not only in the normal reaction product—a secondary alcohol—but also in a diol, a product of the reaction of lithiumbarene with β-hydroxybutyraldehyde, which is probably formed by the action of the secondary alkoxide or a *C*-metallic derivative of barene[38]:

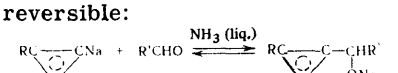


where R = CH_3, C_6H_5.

Sodium derivatives of barenes in liquid ammonia react smoothly only with formaldehyde, to give 92–94% yield of primary alcohols[38]:

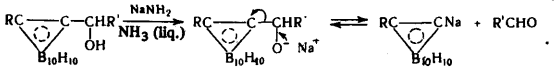


where R = CH_3, C_6H_5. With other aldehydes the yields were substantially lower, mainly because the reaction of sodium derivatives of barenes with aldehydes in liquid ammonia is reversible:

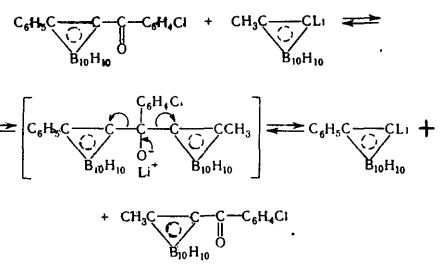


This phenomenon is probably a particular case of the general tendency of the carbon–carbon bond in carbonyl derivatives and alcohols of the barene series to undergo

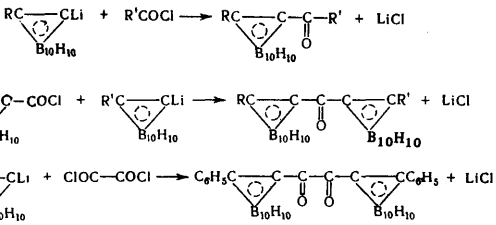
cleavage in the presence of bases[39-41], which is explained by the strong electron-acceptor effect of the barene cage:



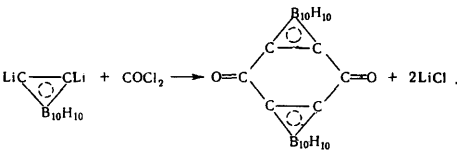
An analogous explanation can be given for the unsuccessful attempts to prepare tertiary alcohols of barenes by the reaction of barenyl-lithium derivatives with barene ketones[42,43]:



For the same reason formation of tertiary alcohols is not observed when lithiumbarenes interact with acid chlorides, the reaction halting at the ketone stage. This has been utilised by Zakharkin and L'vov[42,44] to prepare a large number of ketones of the barene series:

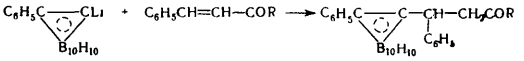


Dilithiumbarene reacts with carbonyl chloride to yield a cyclic diketone[45]:



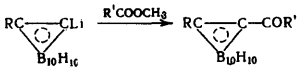
This compound, however, does not react with 1,1-dimethylhydrazine (which would be characteristic of the carbonyl group), owing to the influence of the barenyl cage.

Phenylbarenyl-lithium reacts smoothly with chalcone and with styryl t-butyl ketone in benzene solution to give the corresponding γ-ketones[46]:

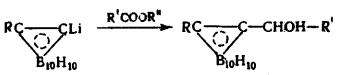


where R = C_6H_5, $C(CH_3)_3$.

Esters react with lithium derivatives of barene to form ketones or secondary alcohols, depending on the structure of the ester. Ketones are formed from the methyl esters of aromatic acids and the methyl and ethyl esters of aliphatic acids, whereas alcohols are the main products from ethyl, propyl, and isopropyl esters of aromatic acids[47]:

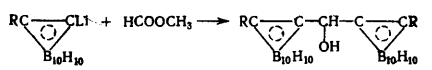


where R = C_6H_5 and R′ = C_6H_5, p-$CH_3C_6H_5$, p-BrC_6H_4; R = CH_3 and R′ = C_6H_5;



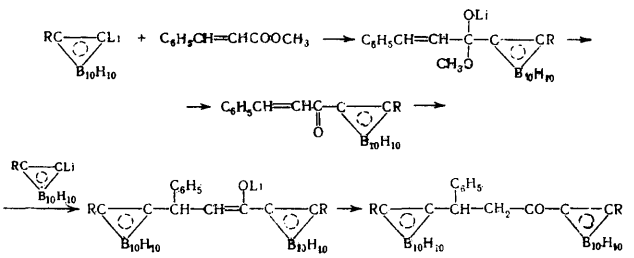
where R = R′ = C_6H_5 and R″ = C_2H_5, C_3H_7; R = CH_3, R′ = C_6H_5, and R″ = C_2H_5.

Lithiumbarenes react with methyl and ethyl formate similarly to Grignard reagents, yielding secondary alcohols containing two barene cages[48]:



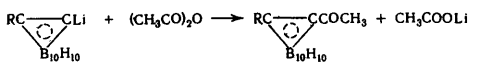
where R = CH_3, C_6H_5.

The reaction between lithium derivatives of barenes and methyl cinnamate takes place in two stages, involving the initial 1,2-addition of the lithiumbarene at the ester carbonyl group to form an $\alpha\beta$-unsaturated barenyl ketone, followed by 1,4-addition of a second lithiumbarene molecule[46]:

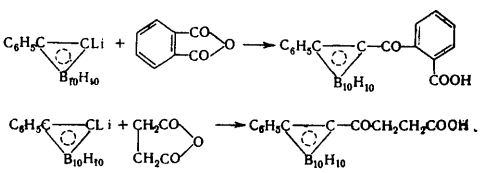


where R = CH_3, C_6H_5.

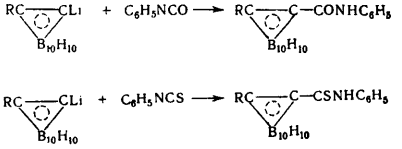
In contrast to the reactions of the usual organolithium compounds, the action of lithiumbarenes on carboxylic anhydrides yields barenyl ketones without the formation of tertiary alcohols[48,49]:



where R = CH_3, C_6H_5. With the anhydrides of dicarboxylic acids lithiumbarenes yield keto-acids of the barene series[48,49]:

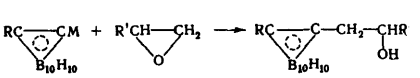


Lithium derivatives of barenes[48] and neobarenes[49] react smoothly with phenyl isocyanate and phenyl isothiocyanate to form the corresponding anilides of the barene- and neobarene-carboxylic and -carbothioic acids:



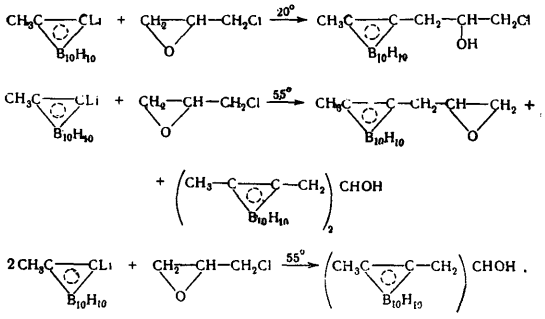
where R = CH_3, C_6H_5.

Lithiumbarenes in ether[16,17] and sodium barenes in liquid ammonia[20,21] react smoothly with α-epoxides to produce high yields of primary and secondary alcohols in which the hydroxyl is in the β-position relative to a carbon atom of the barene cage (the best results are obtained by conducting the reaction with the lithium derivatives in ether)[50]:

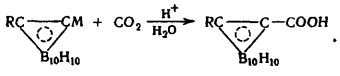


where R = H, CH_3, CH_2:CH, C_6H_5, R′ = H, CH_3, C_6H_5, and

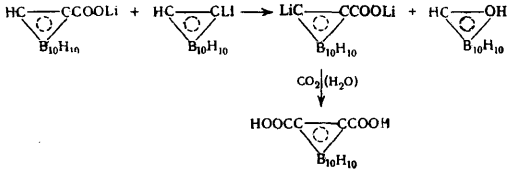
M = Li, Na. In the case of epichlorohydrin in the cold, the oxiran ring is opened without the chlorine atom being affected; when the temperature is raised a mixture of products is formed[50]:



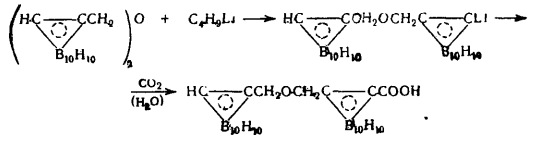
As has already been mentioned (p. 174) magnesium[22,25], lithium[12,15-17], and sodium[19] derivatives of barenes are important starting materials for the preparation of barenecarboxylic acids which are often difficultly accessible:



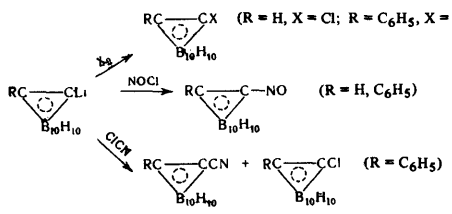
An interesting reaction was observed by Heying et al.[16], who, in attempting to prepare barenecarboxylic acid by treating barene with an equivalent quantity of butyl-lithium and then carboxylating the product, obtained a good yield of barenedicarboxylic acid, as a consequence of the exchange reaction



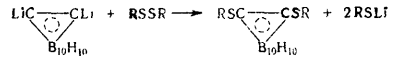
occurring at the instant of carboxylation. These workers explain the enhanced mobility of the hydrogen atom as a proton in lithium barenecarboxylate by the influence of the carboxy-group. Such a phenomenon is not observed in the absence of a carboxyl or when it is remote from the barene cage. Reaction between bisbarenylmethyl ether and an equivalent quantity of butyl-lithium followed by carboxylation yields only the monocarboxylic acid[51]:



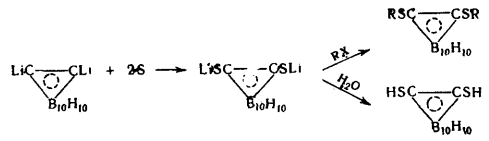
Barenyl-lithium derivatives have been used also for the preparation of halogenobarenes[17,35,44,52], nitrosobarenes[53,54], and cyanobarenes[55]:



Smith et al.[56], starting from dilithiumbarene and neobarene, obtained compounds containing a barene carbon–sulphur bond:

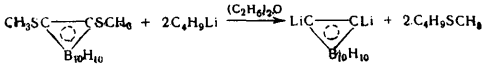


where R = CH_3, C_2H_5, $C_6H_5CH_2$, C_6H_5, $CH_3C_6H_4$;

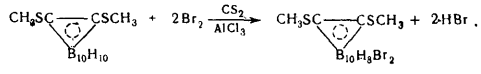


where R = H and X = Cl; R = CH_3 and X = I. Mono-, di-, and tri-*B*-bromobarenes also undergo these reactions. Sulphur dichloride reacts with dilithiumbarene to give polymeric substances of low molecular weight, containing a dithio-bond.

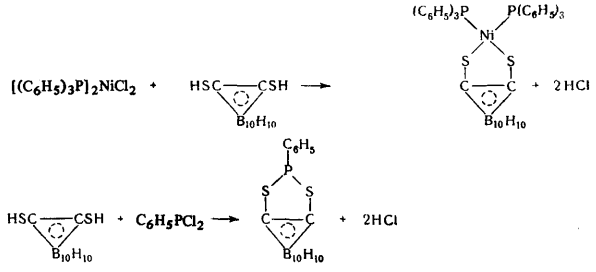
The barene carbon–sulphur bond is cleaved by the action of butyl-lithium. In contrast to dialkyl or mixed alkyl aryl sulphides, this involves nucleophilic attack at the sulphur atom with formation of a carbon–lithium bond[56]:



The electron-acceptor effect of the barene cage on the sulphur atom is shown also in the inability of barenyl sulphides to form sulphonium salts on treatment with bromine in boiling carbon tetrachloride or in carbon disulphide. The addition of aluminium chloride in the latter case merely leads to bromination of the barene cage:

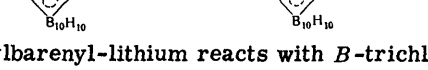


Barenedithiol reacts readily with dichlorobistriphenylphosphinenickel and phenylphosphonous dichloride to form the corresponding five-membered cyclic compounds[56]:

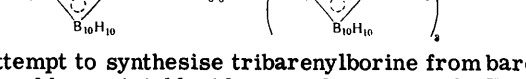


III. BARENYL DERIVATIVES OF BORON

A compound containing a barene carbon–boron bond was first obtained by the action of chlorobisdimethylaminoborine on barenyl-lithium[57]:



n-Butylbarenyl-lithium reacts with *B*-trichloro-*N*-trimethylborazole to give the corresponding barenyl derivative of borazole[57]:

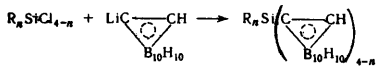


At attempt to synthesise tribarenylborine from barenyllithium and boron trichloride proved unsuccessful[57].

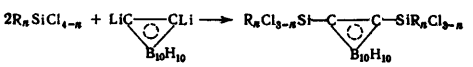
IV. DERIVATIVES OF GROUP IV ELEMENTS

1. Silicon

The specific features of barene compounds permitted the hope that organosilicon polymers containing barenyl radicals would possess unusual properties. This stimulated Papetti, Heying, and their coworkers [58-60] to examine the properties of diverse compounds containing a (barene) carbon–silicon bond, which they synthesised by the action of dilithiumbarenes on various organic and inorganic silicon derivatives containing a silicon–chlorine bond:

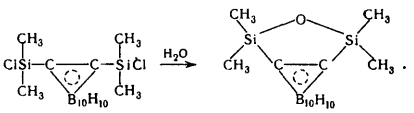


where $n = 2$ and $R = CH_3$; $n = 3$ and $R = CH_3$, C_6H_5;

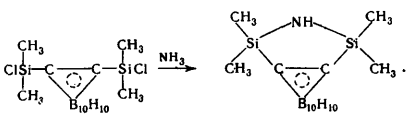


where $n = 0$, 1 and $R = CH_3$; $n = 2$ and $R = CH_3$, C_6H_5.

An attempt was made [58] to convert the resulting bis-chlorodimethylsilylbarene into the corresponding silanol, which was necessary for synthesising a polyorganosiloxane. However, this attempt was unsuccessful, owing to the tendency of the diols to undergo cyclisation with formation of a five-membered siloxane ring containing the two carbon atoms of the barene:

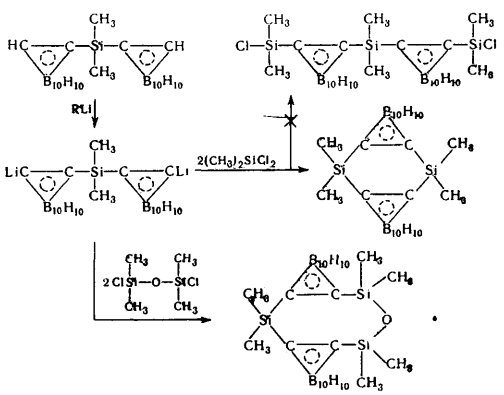


An analogous cyclisation has been observed in the action of ammonia [58]:

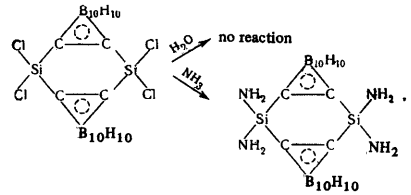


Several workers [16,17,61] have obtained similar compounds containing a ring comprising the two barene carbon atoms together with C–C–C and C–O–C groupings. This ease of formation of five-membered rings is probably due to structural peculiarities in barene (the carbon–carbon distance and the bond angles at a carbon atom).

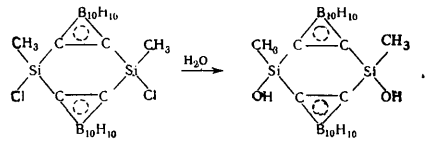
Failure attended also an attempt to obtain an acyclic compound by the action of even excess of dimethyldichlorosilane and tetramethyldichlorosiloxane on the dilithium derivative of dibarenyldimethylsilane [59]:



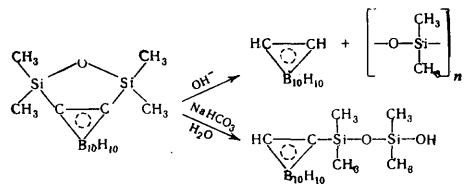
The properties of silicon derivatives of barene are greatly affected also by the strong electron-acceptor action of the barenyl group, as is shown in particular in the stability to hydrolysis of the silicon–chlorine bond in the cyclic tetrachloro-1,4-disilin formed by two barenylidene groups. However ammonia reacts quantitatively with this compound [59]:



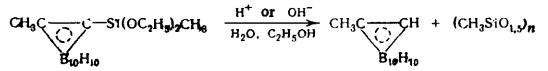
Replacement of one chlorine atom at each silicon atom by a methyl group produces a sharp increase in the ability of the silicon–chlorine bond to be hydrolysed by water, this probably being due to an increase in the ionic character of the bond:



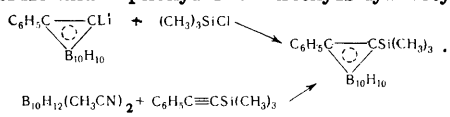
The electron-acceptor influence of the barene cage can explain also the tendency of barenylsilanes to cleavage of the silicon–carbon (barene) bond in the presence of bases [59]:



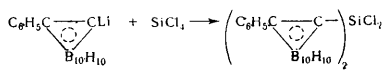
Observations by American chemists [62] indicate that both acids and bases cause rupture of the silicon–carbon bond:



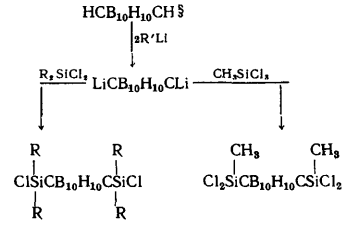
The synthesis of barenylsilanes has been accomplished also by Zakharkin et al. [63] in the case of 1-phenyl-2-trimethylsilylbarene. These workers showed that it was in principle possible to obtain this compound from decaborane–bisacetonitrile and 1-phenyl-2-trimethylsilylacetylene [63]:



Reaction between silicon tetrachloride and phenylbarenyl-lithium (2–4 moles per mole of the halide) results only in the formation of bisphenylbarenyldichlorosilane [64]:

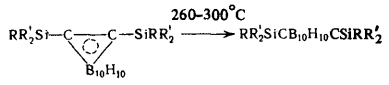


Neobarenylsilanes were obtained [60] in the same way as barenylsilanes:



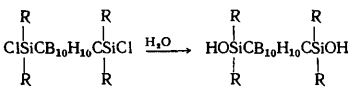
§ Here and subsequently the formula $HCB_{10}H_{10}CH$ will denote neobarene.

where R = CH_3, C_6H_5. It was also noticed[65] that barenylsilanes were able to isomerise into neobarenylsilanes at 260–300°C (barene itself isomerises into neobarene at 500°C [12]):

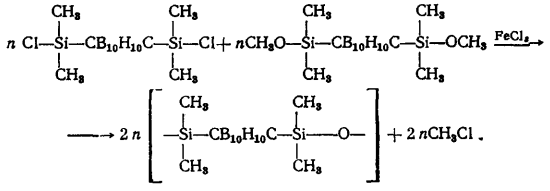


where R = CH_3 and R′ = CH_3, C_6H_5; R = Cl and R′ = C_6H_5; and R = C_6H_5 and R′ = CH_3.

Since the carbon atoms in neobarenes are remote from one another, dihydroxy-derivatives of neobarenylsilanes, unlike their barene analogues, exhibit no tendency to cyclisation[60]:



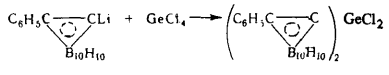
where R = CH_3, C_6H_5. This has enabled neobarenylsilanes to be used in the synthesis of silicon polymers containing the group $-CB_{10}H_{10}C-$ in the polymer chain. However, such polymers could not be synthesised by the hydrolysis of bisdimethylchlorosilylneobarene. The use of various conditions of hydrolysis produced only stable diols[66]. The first polymer of this type was obtained by Papetti et al.[66] by copolymerisation of bisdimethylchlorosilylneobarene with bismethoxydimethylsilylneobarene in the presence of catalytic quantities of iron(III) chloride:



The resulting polysiloxane was a white crystalline substance of molecular weight 16 000. Several polymers containing various combinations of neobarenylene groups and siloxane residues were obtained in the same way.

2. Germanium

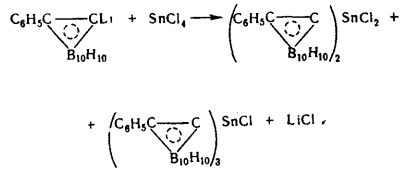
The only barenyl derivative of germanium yet known was obtained by the interaction of phenylbarenyl-lithium and germanium tetrachloride[64]:



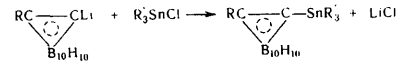
As in the reaction with silicon tetrachloride (see preceding subsection), not more than two chlorine atoms could be replaced owing to steric hindrance due to the bulky barene cage.

3. Tin

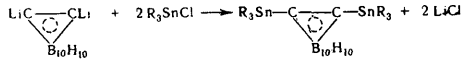
The increase in atomic radius on passing from silicon and germanium to tin makes it possible to obtain a derivative in which tin is attached to three barenyl groups. Thus the reaction between phenylbarenyl-lithium and tin tetrachloride results in a mixture of the corresponding chloride and dichloride[64]:



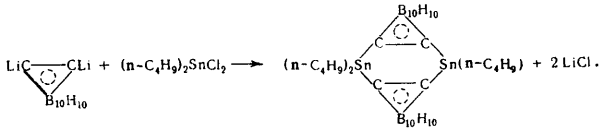
In the absence of steric hindrance, organotin halides are readily alkylated by lithiumbarenes[63,64]:



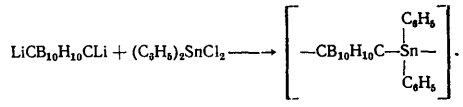
where R = H, C_6H_5, and R′ = n-C_3H_7, C_6H_5. Dilithiumbarene reacts with tri- and di-alkyltin chlorides to give compounds containing two tin atoms in the molecule[64,67]:



where R = n-C_3H_7, C_6H_5; and

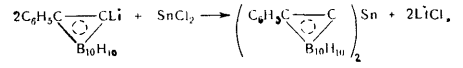


Replacement of dilithiumbarene by dilithiumneobarene in the reaction with dialkyltin dichlorides leads to the formation of—instead of cyclic compounds—polymeric products[68] having molecular weights up to 5750:



A study of the Mössbauer spectra of the organotin compounds obtained has shown[67] that the barenyl group exerts a greater electron-acceptor action on the tin atom than any organic substituent hitherto examined by this method. In its effect on the electronic environment of the tin nucleus it is comparable only with the pentafluorophenyl group. It can be concluded from the Mössbauer spectra that the ionic character of the tin–chlorine and tin–carbon (barene) bonds in trisphenylbarenyltin chloride and bisphenylbarenyltin dichloride is similar to, while the symmetry of the electric field at the tin nucleus is considerably greater than that in the analogous phenyl derivatives, as a consequence of the strong electron-acceptor influence of the barenyl group.

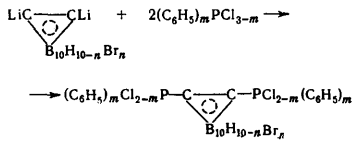
Interaction between phenylbarenyl-lithium and anhydrous tin(II) chloride yields bisphenylbarenyltin, the first derivative of bivalent tin, stable in an inert atmosphere, and showing no tendency to polymerise[67]:



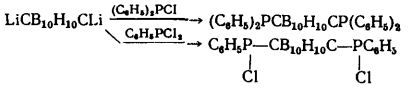
V. DERIVATIVES OF GROUP V ELEMENTS (PHOSPHORUS, ARSENIC, ANTIMONY)

Mixed barenyl(phenyl)phosphines have been obtained by the reaction of phenylchlorophosphines with the dilithium

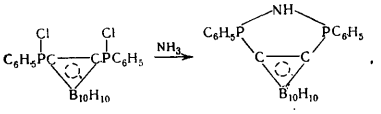
derivatives of barene[69,70], neobarene[71], and *B*-polyhalogenobarenes[30]:



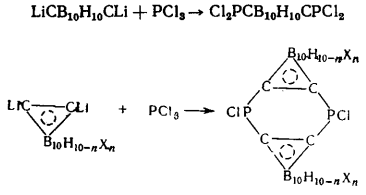
where $n = 0$ and $m = 1, 2$; $n = 1-3$ and $m = 2$; and $n = 2$ and $m = 1$; also



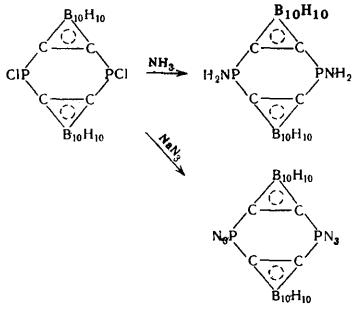
The action of ammonia on *PP'*-dichloro-*PP'*-diphenylbarenylenediphosphine yields a five-membered ring typical of the chemistry of the barenes[69]:



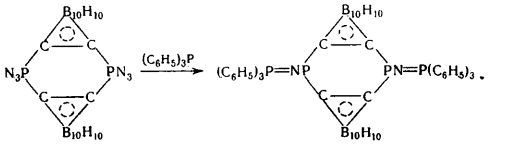
With phosphorus trichloride dilithiumneobarene gives *P*-tetrachloroneobarenylenediphosphine[71], whereas dilithiumbarene gives a six-membered ring containing two phosphorus atoms[30,69,70]:



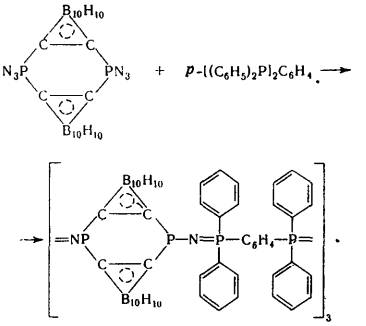
where X = Br, Cl and $n = 0-4$. The chlorine atoms in the resulting compound are readily replaced by the action of ammonia and of sodium azide[69]:



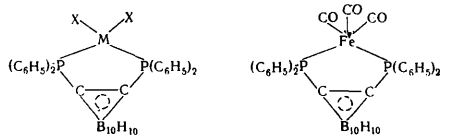
The resulting azido-derivative undergoes two very interesting reactions, the first of which yields a stable phosphine imide derivative[69]:



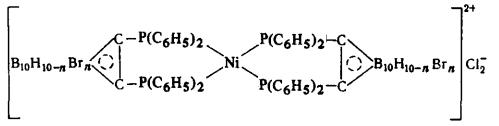
The second reaction[69] gives an oligomer of molecular weight ~ 2500, which has been used as a bonding agent in the manufacture of asbestos materials stable at high temperatures[72]:



Smith[73], and also Zakharkin and Zhigareva[74], discovered that *PP'*-tetraphenylbarenylenediphosphine was able to form stable five-membered chelate complexes with transition metals:

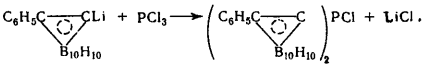


where M = Ni and X = CO, Cl; M = Pd and X = Cl; and also

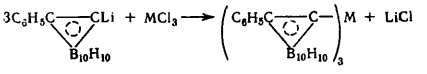


in which $n = 0-3$.

As with barenyl derivatives of Group IV elements, steric hindrance due to the bulky barenyl group is shown in the impossibility of substituting all three chlorine atoms when phenylbarenyl-lithium is treated with phosphorus trichloride[64]:



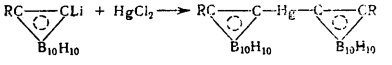
However, the increase in atomic radius on passing to arsenic and antimony compensates for the steric factors, and the halides of these two elements readily form trisubstituted derivatives[64]:



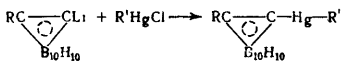
where M = As, Sb.

VI. MERCURY DERIVATIVES

In view of the part played by organomercury compounds in the study of the properties of the metal–carbon bond, the organomercury derivatives of barenes are of great value for an understanding of the peculiarities in the chemical behaviour of the metal–barene carbon bond. They were first obtained by Zakharkin and his coworkers[63,64,75,76] by the action of *C*-lithium derivatives of barenes on mercury(II) chloride or an alkylmercury halide:



where R = H, CH_3, $CH_2:CH$, C_6H_5; or

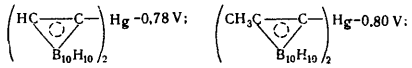


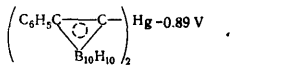
where R = H, CH_3, $CH_2:CH$, C_6H_5 and R′ = CH_3; R = C_6H_5 and R′ = C_6H_5, ferrocenyl.

Symmetrical barenylmercury compounds are distinguished by great stability, remaining unchanged even on prolonged heating at 300–350°C. The unsymmetrical compounds RHgR′ (in which R and R′ are barenyl radicals) do not tend to disproportionate into R_2Hg and R'_2Hg even in the melt (150–200°C) [75].

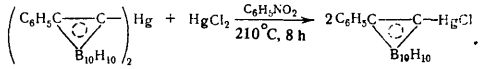
During the action of phenylbarenyl-lithium on mercury(II) chloride the reaction mixture contains no phenylbarenylmercury chloride, which is an unusual feature in the chemistry of organomercury compounds. Bisphenylbarenylmercury is immediately formed, while the excess of mercuric chloride does not react. An analogous phenomenon is observed with vinyl- and methyl-barenyl-lithium. Thus the alkylbarenylmercury chloride is very readily alkylated in comparison with the initial mercury chloride, and this has no analogy in organomercury chemistry.

The strong electron-acceptor effect of the barenyl group towards the mercury atom is confirmed by an examination of barenylmercury compounds by polarographic reduction. Some half-wave potentials obtained (in dimethylformamide) are indicated below [76]



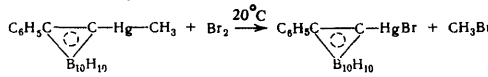


With the mercury derivatives of barenes, especially the symmetrical compounds, cleavage of the carbon–mercury bond under the influence of electrophilic reagents [hydrogen chloride, bromine, mercury(II) chloride], which is so common in the chemistry of ordinary organomercury compounds, goes either with difficulty or not at all. Thus phenylbarenylmercury chloride is not formed by the prolonged boiling of bisphenylbarenylmercury with mercury(II) chloride in alcohol. It was successfully obtained only when the reactants were heated in boiling nitrobenzene (for 8 h) [75,76]:

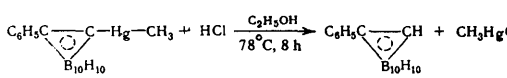


The mercury–carbon bond in symmetrical barenylmercury compounds is not ruptured by the action of bromine in boiling dichloromethane and benzene or on boiling with alcoholic hydrogen chloride solution (for 20 h).

When bromine acts on methyl(phenylbarenyl)mercury in the cold, it is only the mercury–methyl bond which is broken. The mercury–carbon (barene) bond remains unchanged, phenylbarenylmercury bromide being formed in almost quantitative yield [76]:

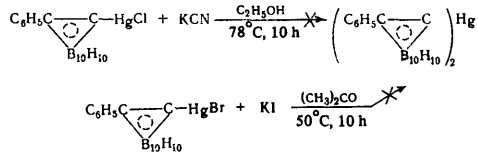


However, the action of alcoholic hydrogen chloride on methyl(phenylbarenyl)mercury produces rupture of the mercury–carbon (barene) bond with formation of phenylbarene [63]:



The above results indicate that cleavage of the mercury–carbon bond proceeds by different mechanisms under the influence of bromine and of proton acids.

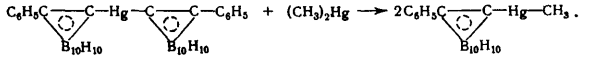
Phenylbarenylmercury chloride and bromide were found to be stable to the action of such strong symmetrising agents as potassium cyanide and iodide [76]:



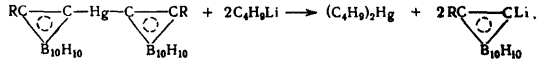
One reason for the anomalous behaviour of barenylmercury compounds in reactions involving electrophilic substitution at a barene carbon atom is probably the unusual valency state of the six-coordinated barene carbon atom, which is unable to form a cyclic transition state, as this would require the unlikely and unprecedented increase in the coordination number of carbon to seven. Furthermore, formation of such a transition complex is prevented also by steric hindrance due to the icosahedral barene cage. It must also be reckoned that the barene cage will exert a strong electron-acceptor influence, preventing localisation of a negative charge on a barene carbon atom.

Nothing that has been stated above excludes the possibility, however, of a unimolecular reaction (S_E1), which probably occurs if reaction with the electrophilic reagent does take place [reaction with mercury(II) chloride in boiling nitrobenzene, protolysis].

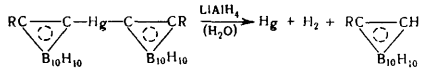
Under severe conditions (230°C for 9 h) even dimethylmercury reacts with bisphenylbarenylmercury, yielding methyl(phenylbarenyl)mercury [77]:



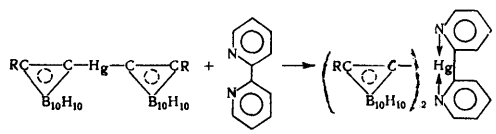
Cleavage of the mercury–carbon (barene) bond occurs far more readily during nucleophilic attack at the mercury atom. Thus symmetrical barenyl derivatives of mercury react with such nucleophilic reagents as butyl-lithium even in the cold, with the formation of products of the exhaustive exchange of radicals [77]:



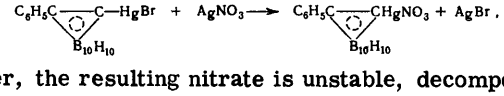
Bismethylbarenyl- and bisphenylbarenyl-mercury are easily reduced by lithium tetrahydroaluminate [77]:



The coordinative unsaturation of a mercury atom attached to two barenyl radicals is so great that even symmetrical barenylmercury compounds readily form complexes with 2,2′-bipyridyl [77]:



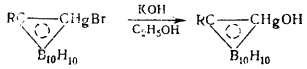
The halogen in barenylmercury halides is replaced by the action of an aqueous–alcoholic solution of silver nitrate [77]:



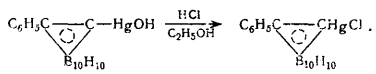
However, the resulting nitrate is unstable, decomposing

even at room temperature with the evolution of oxides of nitrogen.

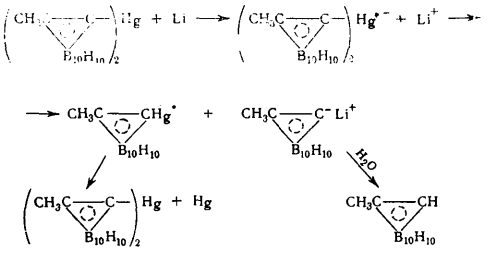
Alcoholic alkali acts on barenylmercury bromides, the bromine being easily replaced by hydroxyl[77]:



where R = CH_3, C_6H_5. The resulting hydroxides are difficultly identifiable substances which are unstable in air. Phenylbarenylmercury hydroxide reacts with hydrochloric acid to give phenylbarenylmercury chloride:

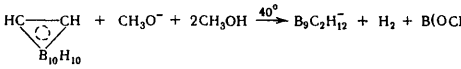


Symmetrical barenyl derivatives of mercury, which are stable towards metals (lithium, aluminium) when heated in an inert medium (xylene), react with lithium in dimethoxyethane even in the cold, as has been shown with bismethylbarenylmercury[77]. The rate of the process is probably determined by electron transfer from the metal to a molecule of the organomercury compound:

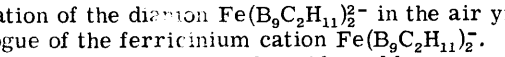


VII. ORGANOMETALLIC DERIVATIVES OF DICARBAUNDECABORANE

Treatment of barene with alcoholic alkali results in its partial cleavage with the formation of an anion of dicarbaundecaborane[78]:



By using this anion, Hawthorne and his coworkers were able to synthesise a series of "sandwich" derivatives, which are analogues of the cyclopentadienyl compounds of transition metals (iron, manganese, rhenium, cobalt). The first member of this series was obtained[79] by reaction between iron(II) chloride and the doubly charged anion $B_9C_2H_{11}^{2-}$, formed from $B_9C_2H_{12}^-$ by the action of metallic sodium or of sodium hydride:



Oxidation of the dianion $Fe(B_9C_2H_{11})_2^{2-}$ in the air yields the analogue of the ferricinium cation $Fe(B_9C_2H_{11})_2^-$. Salts of this anion are stable towards acids and bases, and remain unchanged when heated to 300°C.

When a mixture of cyclopentadienylsodium and the disodium salt of the anion $B_9C_2H_{11}^{2-}$ in tetrahydrofuran is boiled with iron(II) chloride, the corresponding mixed derivative π-$C_5H_5Fe(\pi$-$B_9C_2H_{11})^-$ is formed[80]. Study of the crystal structure of this compound showed[81] that the iron atom is approximately at the same distance from the five carbon atoms of the cyclopentadienyl ring (2.07 Å) as from the two carbon atoms (2.04 Å) and the three boron atoms (2.09 Å) of the dicarbaundecaborane. This and several other investigations[79,80,82] have enabled the structure of the above compounds to be established (Fig. 2).

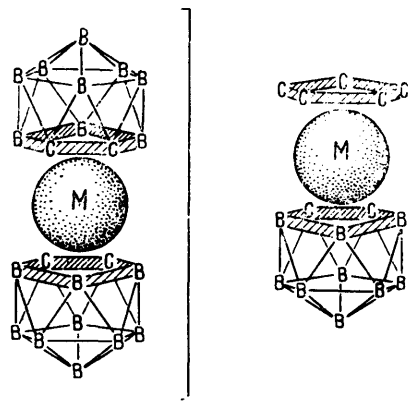


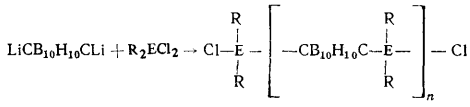
Figure 2. Structure of "sandwich" derivatives of the dicarbaundecaborane anion.

Sandwich derivatives of other metals have also been prepared[83-86]—$(B_9C_2H_{11})Mn(CO)_3^-$, $(B_9C_2H_{11})Re(CO)_3^-$, $(B_9C_2H_{11})_2Co^-$, $(C_5H_5)Co(B_9C_2H_{11})$, and $[\pi$-$(C_6H_5)C_4]Pd$.$[\pi$-$B_9C_2H_{11}]$.

Thus the organoelementary chemistry of these novel non-coplanar aromatic compounds—the barenes—has accumulated within a short time considerable and interesting information. Work on these lines is being vigorously prosecuted.

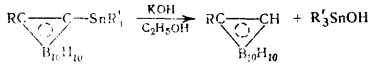
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Several interesting researches have recently been done on the barenyl derivatives of Group IV elements. Thus some American chemists[89] have prepared germanium and tin polymers containing a neobarene grouping in the main chain, and having molecular weights up to 9000:

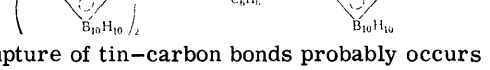


where E = Ge, Sn and R = CH_3, C_6H_5.

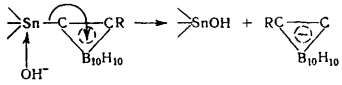
Bregadze and Okhlobystin have shown[90] that the tin–carbon bond in barenyl derivatives of tin is easily cleaved by aqueous and alcoholic solutions of alkalis, with formation of the corresponding barenes and organotin hydroxides:



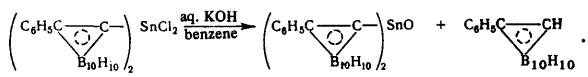
where R = C_6H_5, H and R′ = C_3H_7, C_6H_5; also



The rupture of tin–carbon bonds probably occurs by direct nucleophilic attack on the tin atom, with as a consequence heterolytic dissociation and formation of a barenyl anion:



The lability of the tin–carbon (barene) bond under nucleophilic attack is so great that, when a benzene solution of bisphenylbarenyltin dichloride is treated with aqueous alkali, there is competitive cleavage of tin–carbon and tin–chlorine bonds:



The tin–carbon bonds in the dichloride undergo cleavage even during chromatography on aluminium oxide, which results in the formation of phenylbarene.

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U.D.C. 547.257.1 + 546.711

The Chemistry of Manganese Carbonyl

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