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ORGANOMERCURIC DERIVATIVES OF BARENES

SOME FEATURES OF ELECTROPHILIC SUBSTITUTION AT A HEXA-COORDINATED BARENIC CARBON ATOM

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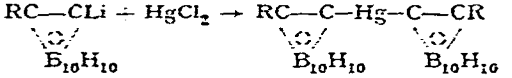
The most striking feature of the icosahedral structure of barenes ("carboranes-10")[1,2] is the unusual co-ordination state of the two carbon atoms, each of them being linked with *six* other atoms. The C–C bond (1.64–1.70 Å)[3,4] is not inherently similar to any other bond in the whole of organic chemistry. From the structural aspect, the carbon atoms are essentially identical with boron atoms. These circumstances combine with the strong electron-withdrawing power of the bulky barene nucleus, to give the C-functional derivatives of barenes unusual properties.

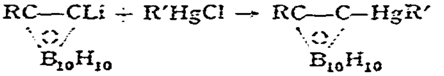
An investigation of the organomercuric derivatives of barenes would, we believed, resolve some features of electrophilic substitution at a barenic carbon atom because it would be possible to take advantage of traditional methods of organomercuric chemistry[5].

The necessary compounds were obtained by means of the general procedures previously described[6–8], *e.g.* by the action of the organolithium derivatives of barenes on mercuric chloride or alkylmercuric chloride:



$$\underset{B_{10}H_{10}}{RC{-}CLi} + HgCl_2 \rightarrow \underset{B_{10}H_{10}}{RC{-}C}{-}Hg{-}\underset{B_{10}H_{10}}{C{-}CR}$$

R=H, CH_3, CH_2=CH, C_6H_5



$$\underset{B_{10}H_{10}}{RC{-}CLi} + R'HgCl \rightarrow \underset{B_{10}H_{10}}{RC{-}C}{-}HgR'$$

R=H, CH_3, CH_2=CH C_6H_5; R'=CH_3.
R=C_6H_5; R'=C_6H_5, ferrocenyl

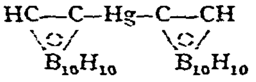
The synthesis of these compounds itself proceeds unusually. The addition of, say, phenylbarenyllithium to twice the theoretical amount of mercuric chloride in benzene appears to lead to the formation of symmetrical bis(phenylbarenyl)mercury. No trace of phenylbarenylmercuric chloride can be detected and the surplus mercuric chloride remains unchanged. Vinylbarenyllithium and methylbarenyllithium react in the same manner. Phenylbarenylmercuric chloride shows no tendency to symmetrization (see below). Hence, the source of the above anomaly does not lie in the fast reaction:

$$2\underset{B_{10}H_{10}}{RC{-}CHgCl} \not\rightleftharpoons \underset{B_{10}H_{10}}{RC{-}C}{-}Hg{-}\underset{B_{10}H_{10}}{C{-}R} + HgCl_2$$

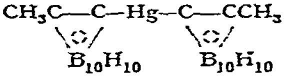
and phenylbarenylmercuric chloride is alkylated more readily than mercuric chloride. The last phenomenon seems, so far, to be unique in organomercuric chemistry.

It may be that this effect is related to a decrease in the ionic character of the Sn–Cl bonds in barene derivatives of tin, when compared with the appropriate phenyl compounds; this has been fairly well established by gamma ray resonance spectroscopy[9].

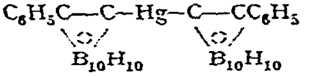
The barenyl groups in the mercuric derivatives of barenes (as in the tin compounds) are strong electron acceptors towards the metal atom. This is completely borne out by polarographic reduction measurements of certain barenylmercuric compounds. The half-wave potentials obtained (in dimethylformamide) are as follows:



$$\underset{B_{10}H_{10}}{\underset{\backslash O/}{HC-C}}-Hg-\underset{B_{10}H_{10}}{\underset{\backslash O/}{C-CH}} \quad E_{1/2} = -0.78\ V$$



$$\underset{B_{10}H_{10}}{\underset{\backslash O/}{CH_3C-C}}-Hg-\underset{B_{10}H_{10}}{\underset{\backslash O/}{C-CCH_3}} \quad -0.80\ V$$



$$\underset{B_{10}H_{10}}{\underset{\backslash O/}{C_6H_5C-C}}-Hg-\underset{B_{10}H_{10}}{\underset{\backslash O/}{C-CC_6H_5}} \quad -0.89\ V$$

cf. $[(CO)_3MnC_5H_4]_2Hg$, −2.30 V; $(C_6H_5)_2Hg$, −2.60 V; $(C_5H_5FeC_5H_4)_2Hg$, >−2.80 V (Ref. 10).

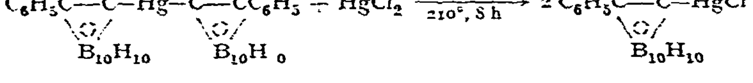
It can be seen that barenic compounds are reduced at substantially lower potentials than simpler compounds of the R_2Hg type.

Symmetrical dibarenylmercuric compounds are distinguished by high thermal stability; they are unchanged even on prolonged heating at 300–350°. Mixed compounds, RHgR′ (R = barenyl radical), have no tendency to disproportionate to R_2Hg and $R_2'Hg$ at the melting point (150–200°).

In spite of the fact that the splitting of the C–Hg bond by the action of electrophiles such as HCl, Br_2 and $HgCl_2$ is easily accomplished for ordinary mercury diaryls and dialkyls, the related reactions of the barenic compounds only lake place, if at all, under severe conditions. Symmetrical compounds, *e.g.* bis(phenylbarenyl)mercury, are especially stable towards these reagents. Thus, the reaction

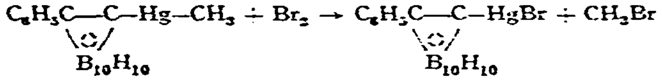
$$R_2Hg + HgCl_2 \rightarrow 2\ RHgCl$$

usually takes place very easily, but bis(phenylbarenyl)mercury is quite stable on continuous refluxing with mercuric chloride in alcohol. We succeeded in obtaining phenylbarenylmercury chloride only when boiling nitrobenzene was used as a solvent (8 h) and even then the yield of the chloride was not higher than 20 %:



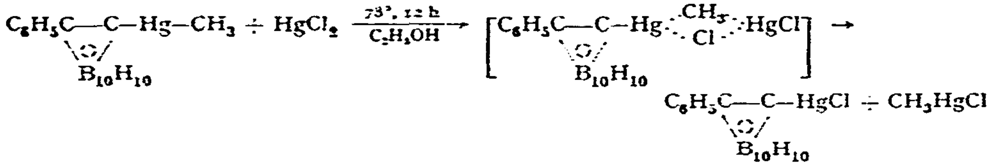
$$\underset{B_{10}H_{10}}{\underset{\backslash O/}{C_6H_5C-C}}-Hg-\underset{B_{10}H\ _{0}}{\underset{\backslash O/}{C-CC_6H_5}} + HgCl_2 \xrightarrow[210°,\ 8\ h]{C_6H_5NO_2} 2\ \underset{B_{10}H_{10}}{\underset{\backslash O/}{C_6H_5C-C}}-HgCl$$

When bis(phenylbarenyl)mercury is refluxed with bromine for 10 h in dichloromethane or benzene, it remains unchanged. Bromine breaks only the Hg–CH_3 bond in methyl(phenylbarenyl)mercury, the Hg–barene bond is unaffected:



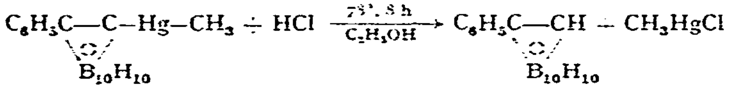
$$\underset{B_{10}H_{10}}{C_6H_5C\text{—}C}\text{–}Hg\text{–}CH_3 + Br_2 \rightarrow \underset{B_{10}H_{10}}{C_6H_5C\text{—}C}\text{–}HgBr + CH_3Br$$

Seemingly, mercuric chloride reacts in the same manner:



$$\underset{B_{10}H_{10}}{C_6H_5C\text{—}C}\text{–}Hg\text{–}CH_3 + HgCl_2 \xrightarrow[C_2H_5OH]{78°,\ 12\ h} \left[\underset{B_{10}H_{10}}{C_6H_5C\text{—}C}\text{–}Hg\overset{CH_3}{\underset{Cl}{\cdots}}HgCl\right] \rightarrow \underset{B_{10}H_{10}}{C_6H_5C\text{—}C}\text{–}HgCl + CH_3HgCl$$

Rupture of the Hg–C bond in bis(phenylbarenyl)mercury scarcely takes place in refluxing with alcoholic hydrogen chloride for 10 h. Nevertheless, it would be wrong to claim that the Hg–barene bond is always chemically inert. The action of alcoholic hydrogen chloride on methyl(phenylbarenyl)mercury gives phenylbarene but not methane:

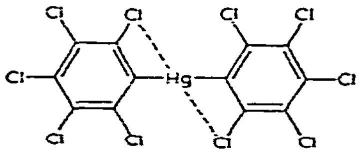


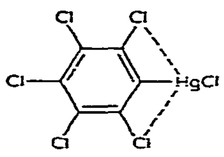
$$\underset{B_{10}H_{10}}{C_6H_5C\text{—}C}\text{–}Hg\text{–}CH_3 + HCl \xrightarrow[C_2H_5OH]{78°,\ 8\ h} \underset{B_{10}H_{10}}{C_6H_5C\text{—}CH} + CH_3HgCl$$

It follows that in the system C–Hg–barene, bromine breaks the C–Hg bond whereas hydrogen chloride attacks the Hg–barene bond. This enables a clear distinction to be drawn between the mechanism of the splitting of C–Hg bond by the action of bromine and the mechanism of protolysis.

Attempts to explain the unusual properties of Hg–barene bonds prompt us to compare the substances under discussion with the pentafluoro-[11] and pentachlorophenyl[12] derivatives of mercury which have recently been described. Pentafluoro- and pentachlorophenylmercury compounds, like the barene derivatives, are thermally very stable. Mixed compounds have no tendency to symmetrization. Bis(pentafluorophenyl)mercury does not react with hydrogen chloride and reacts with bromine only with difficulty. Methyl(pentafluorophenyl)mercury, however, reacts with hydrogen chloride liberating pentafluorobenzene[11]. The only evident reason for this similarity is the strong and almost equal electronegativity of the groups considered[9] although this in itself does not account for all the facts.

In bis(pentachlorophenyl)mercury[12], for example, there is a coordination interaction between the mercury atom and chlorine atoms in the *ortho*-positions. ^{35}Cl NQR data[13] show that this interaction is considerable:

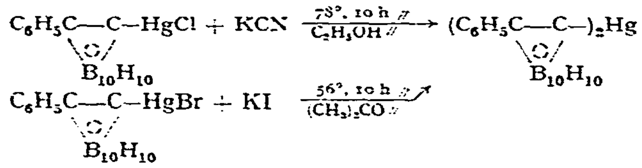




Because of this, the coordinating power of the mercury atom is partly occupied and the capacity of mercury to take part in the bridge transition states is therefore reduced.

With the mercury derivatives of barenes, a strong interaction of this type is impossible. In this case, the hexa-coordinated carbon atom opposes the formation of a cyclic transition state; in the barenylmercuric compounds, carbon has a coordination number of six even in the non-reacting molecule. In order to form a coordination cyclic complex in the transition state, the carbon must increase its coordination number to seven. Such an increase has no analogy in organic chemistry and the transition complex is not likely to be formed. In addition, it should not be overlooked that the icosahedral barenic nucleus brings into play appreciable steric hindrance. The effect of steric factors on the scission of the C–Hg bond may be important as was demonstrated for α-(chloromercury)camphenilone[14].

Our hypothesis regarding the anomalous properties of the Hg–barene bond may explain why phenylbarenylmercuric chloride and bromide are resistant to the action of symmetrizing agents such as potassium iodide and potassium cyanide:

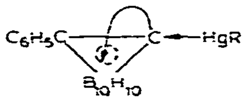


$$\underset{B_{10}H_{10}}{C_6H_5C\text{—}C}\text{—}HgCl + KCN \xrightarrow[C_2H_5OH\ /\!/]{78^\circ,\ 10\ h\ /\!/} (\underset{B_{10}H_{10}}{C_6H_5C\text{—}C}\text{—})_2Hg$$

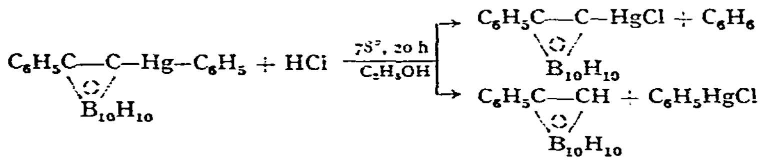
$$\underset{B_{10}H_{10}}{C_6H_5C\text{—}C}\text{—}HgBr + KI \xrightarrow[(CH_3)_2CO\ /\!/]{56^\circ,\ 10\ h\ /\!/}$$

The impossibility of forming the cyclic transition state by means of coordination does not rule out an attack by a free cation (the reaction of a cation-dipole type, S_E1). It is likely that such a reaction explains an apparent electrophilic substitution (the reaction with $HgCl^+$ in boiling nitrobenzene; protolysis).

It is essential to take into account the fact that the barenyl radical is a strong electron acceptor. The stability of the C–Hg bonds in bis(phenylbarenyl)mercury to the action of alcoholic hydrogen chloride is accounted for by the "sucking" of electrons *into* the barene icosahedron. This effect leads to reduction in electron density on the barenic carbon:



In methyl(phenylbarenyl)mercury, this electron absorption is compensated, to a certain degree, by electron donation from the methyl group *via* the mercury atom. If the methyl is replaced by phenyl, this compensation occurs to a lesser degree. Then the reaction proceeds more slowly and takes simultaneously two courses:



$$\underset{B_{10}H_{10}}{C_6H_5C\text{—}C}\text{—}Hg\text{—}C_6H_5 + HCl \xrightarrow[C_2H_5OH]{78^\circ,\ 10\ h} \begin{cases} \underset{B_{10}H_{10}}{C_6H_5C\text{—}C}\text{—}HgCl + C_6H_6 \\ \underset{B_{10}H_{10}}{C_6H_5C\text{—}CH} + C_6H_5HgCl \end{cases}$$

It is possible to conclude from the above discussion that the major considerations that define the character of electrophilic substitution at a barenic carbon atom are as follows.

(1) The unusual valency state of the hexa-coordinated barenic carbon atom.
(2) Steric hindrance that appears because of the icosahedral barene nucleus.
(3) The ability of the barene system to accept electrons.

EXPERIMENTAL

Phenylbarene[*]

Dimethylaniline (24.2 g, 0.2 mole) and phenylacetylene (11.2 g, 0.11 mole) were added to 100 ml of a toluene solution of decaborane (12.2 g, 0.1 mole). The evolution of hydrogen was observed even at room temperature. The mixture was heated, with stirring, at 40–45° for 4–5 h and then at 100° until evolution of hydrogen ceased (7–8 h). The solution was cooled, decanted from the residue, washed with dilute (1:3) hydrochloric acid (100 ml) and dried over anhydrous calcium chloride. The residue, after the removal of solvent, was treated with boiling hexane. The cooled hexane solution was passed through a column containing alumina powder. The hexane was removed by vacuum distillation to give pure phenylbarene (19.5 g, 88 % yield), m.p. and mixed m.p. 65–66° (lit.[15] m.p. 66.5°). Recrystallization from hexane did not significantly change the melting point (66–66.5°).

Phenyl(phenylbarenyl)mercury

30 ml of dry ether was added to a solution of phenylbarenyllithium (from 0.01 mole phenylbarene in 50 ml benzene). The mixture was cooled to 5° and 0.009 mole of phenylmercuric chloride was added gradually with vigorous stirring. After the mixture had been heated for 5 h at 45–50°, it was cooled and treated with 20 ml of dilute (1:4) hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were washed with water and dried over $MgSO_4$. After the solvent had been removed under vacuum, the residue was recrystallized from benzene/isooctane mixture to yield 3.2 g (71 %) of phenyl(phenylbarenyl)mercury, m.p. 187–189°. (Found: C, 33.12; H, 4.01. $C_{14}H_{20}B_{10}Hg$ calcd.: C, 33.83; H, 4.06%.)

Methyl(methylbarenyl)mercury

The above procedure was used. From 0.05 mole of methylbarenyllithium and 0.05 mole of methylmercuric chloride, 14.5 g (78%) of methyl(methylbarenyl)mercury was obtained, m.p. 167–167.5° (from heptane). (Found: C, 13.14; H, 4.33; B, 29.04; Hg, 53.59. $C_4H_{16}B_{10}Hg$ calcd.: C, 12.88; H, 4.32; B, 29.01; Hg, 53.79 %.)

Ferrocenyl(phenylbarenyl)mercury

Ferrocenylmercuric chloride, obtained by the direct mercuration of ferrocene[16] was added to a solution of phenylbarenyllithium (from 0.015 mole phenylbarene) in 80 ml of benzene. The standard treatment of the reaction mixture gave 2.0 g (30 %) of ferrocenyl(phenylbarenyl)mercury, m.p. 137–139° (from isooctane). (Found: C, 34.30; H, 4.10; B, 17.38. $C_{18}H_{24}B_{10}FeHg$ calcd.: C, 35.73; H, 4.00; B, 17.88 %.)

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[*] This method gave a higher yield than the one described earlier[15].

Phenylbarenylmercuric chloride

(1) A mixture of bis(phenylbarenyl)mercury[7] (0.05 mole), mercuric chloride (0.05 mole) and 30 ml of nitrobenzene was boiled under reflux (8 h). After the solvent had been removed, the residue was extracted with benzene. The benzene extract was evaporated to dryness and the residue sublimed in vacuum (1 mm, 100°) to yield 0.9 g (20%) of phenylbarenylmercuric chloride, m.p. 188–189°. (Found: C, 21.22; H, 3.50; B, 23.39 $C_8H_{15}B_{10}ClHg$ calcd.: C, 21.10; H, 3.32; B, 23.78 %.)

(2) The same product was also obtained when equimolar quantities of methyl(phenylbarenyl)mercury and mercuric chloride were boiled in ethanol (20 h). The yield was 43% of the theoretical.

Phenylbarenylmercuric bromide

0.02 mole of bromine was added to a solution of methyl(phenylbarenyl)mercury (0.02 mole) in benzene at 5°. The mixture was allowed to reach room temperature. The solution slowly decolourised in 12 h. No trace of methylmercuric bromide was apparent at any time. After the benzene had been removed, the residue was recrystallized from heptane to yield 9.0 g (90 %) of phenylbarenylmercuric bromide, m.p. 173–174°. (Found: C, 19.81; H, 3.21; B, 21.57; Hg, 39.25. $C_8H_{15}B_{10}BrHg$ calcd.: C, 19.22; H, 3.02; B, 21.64; Hg, 40.12 %.)

The reaction of vinylbarenyllithium with excess mercuric chloride

A benzene solution (60 ml) of vinylbarenyllithium prepared from 6.8 g (0.04 mole) of vinylbarene was added with stirring to a suspension of excess mercuric chloride (16.2 g, 0.06 mole) in ether. The mixture was allowed to reflux for 10 h with stirring, cooled and filtered. The solid residue was washed with cold water and after drying, 10.1 g of unreacted mercuric chloride was recovered. The ether/benzene solution was evaporated and the residue recrystallized from cyclohexane to give 6.1 g (56%) of bis(vinylbarenyl)mercury, m.p. and mixed m.p. 153–154° (lit.[7] m.p. 153.5–154°). No trace of vinylbarenylmercuric chloride was obtained.

Cleavage of methyl(phenylbarenyl)mercury with hydrogen chloride

A saturated solution (6 ml) of gaseous HCl in ethanol was added to methyl(phenylbarenyl)mercury (0.04 mole) in dry ether. The mixture was boiled for 8 h and then cooled. The formation of phenylbarene was observed (thin-layer chromatography with Al_2O_3). The solvent was removed and phenylbarene was extracted from the residue with hexane. Phenylbarene was obtained in almost quantitative yield (0.7 g), m.p. and mixed m.p. 60–63°. The hexane-insoluble residue was methylmercuric chloride (1 g; quantitative yield), m.p. and mixed m.p. 168–169° (lit. m.p. 170°).

Cleavage of phenyl(phenylbarenyl)mercury with hydrogen chloride

Phenyl(phenylbarenyl)mercury does not react with alcoholic HCl on refluxing for 20 h (thin-layer chromatography). A stream of dry hydrogen chloride was passed through a refluxing solution of this substance in a mixture of benzene and ether (3:1). After 5 h, phenylbarene, phenylmercuric chloride and phenylbarenylmercuric chloride were detected by means of chromatography on Al_2O_3. None of the initial compound remained after 20 h.

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SUMMARY

(1) Organomercuric derivatives of barenes react with electrophilic reagents (*e.g.* hydrogen chloride, bromine, mercuric chloride), if at all only under very vigorous conditions.

(2) Barenylmercuric chlorides of the RHgCl type are resistant to the action of common symmetrizing agents but are alkylated more readily than mercuric chloride.

(3) The major properties that define the character of electrophilic substitution at a barenic carbon atom are the unusual coordination state of barenic carbon, steric hindrance and the ability of the barenic nucleus to accept electrons.

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