ARYL-(9-m-CARBORANYL)HALONIUM SALTS

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We have recently described the first carborane halonium compounds, namely, phenyl-(9-o-carboranyl)iodonium, phenyl-(9-m-carboranyl)iodonium [1], phenyl-(2-p-carboranyl)iodonium [2], bis(9-m-carboranyl)bromonium, and phenyl-(9-m-carboranyl)bromonium salts [3]. In a continuation of these studies, we report the synthesis of a number of new aryl-(9-m-carboranyl)halonium compounds, in which the benzene ring contains a substituent in addition to the carboranylhalonium group.

The previously reported oxidative condensation of 9-iodo-m-carborane with benzene [1] may be extended to several substituted benzenes. Thus, for example, syntheses are reported for 4-fluorophenyl-(9-m-carboranyl)iodonium (I) and 3-nitrophenyl-(9-m-carboranyl)iodonium tetrafluoroborides (II):

$$9\text{-}m\text{-}C_2H_2B_{10}H_9I + PhF \xrightarrow[7\ h]{[O],\ H^+,\ BF_4^-} 9\text{-}m\text{-}C_2H_2B_{10}H_9\overset{+}{I}C_6H_4F\text{-}p\ \ B\bar{F}_4 \quad \text{(I), } 83\%$$

$$9\text{-}m\text{-}C_2H_2B_{10}H_9I + PhNO_2 \xrightarrow[58\ h]{[O],\ H^+,\ BF_4^-} 9\text{-}m\text{-}C_2H_2B_{10}H_9\overset{+}{I}C_6H_4NO_2\text{-}m\ \ B\bar{F}_4 \quad \text{(II), } 10\%$$

The reaction rate, yield of the desired product, and position of the substituents support our proposed mechanism for the oxidative condensation [1], which, as in aromatic compounds [4], entails the formation of an iodoso derivative and electrophilic attack of the protonated form of this intermediate on the aromatic ring:

$$9\text{-}m\text{-}C_2H_2B_{10}H_9I \xrightarrow{[O]} 9\text{-}m\text{-}C_2H_2B_{10}H_9IO \xrightarrow{H^+} 9\text{-}m\text{-}C_2H_2B_{10}H_9\overset{+}{\widehat{IOH}} \xrightarrow{ArH} 9\text{-}m\text{-}C_2H_2B_{10}H_9\overset{+}{I}Ar + H_2O$$

Unfortunately, this method did not yield carboranyliodonium derivatives of arenes containing electron-donor substituents since *in situ* oxidation of the iodocarborane to the iodosocarborane requires vigorous conditions, featuring a high concentration of a strong oxidizing agent in the presence of concentrated sulfuric acid, under which benzene derivatives with electron-donor groups readily undergo extensive oxidation. Thus, such cases require the introduction of an independently prepared iodosocarborane such as previously described 9-m-carboranyliodoso-bis(trifluoroacetate) [1] into the reaction with the arene. Thus, in the present work, high yields of mesityl-(9-m-carboranyl)iodonium (III) and 4-methoxyphenyl-(9-m-carboranyl)iodonium tetrafluoroborides (IV) were obtained:

$$9\text{-}m\text{-}C_2H_2B_{10}H_9I(O_2CCF_3)_2 \left| \begin{array}{l} \xrightarrow[BF_4^-]{C_6H_5OCH_3} 9\text{-}m\text{-}C_2H_2B_{10}H_9\overset{+}{I}C_6H_4OCH_3\text{-}p\ \ B\bar{F}_4 \quad \text{(IV), } 84\% \\ \xrightarrow[BF_4^-]{1,3,5\text{-}(CH_3)_3C_6H_3} 9\text{-}m\text{-}C_2H_2B_{10}H_9\overset{+}{I}C_6H_2(CH_3)_3\text{-}2,4,6\ \ B\bar{F}_4 \quad \text{(III), } 84\% \end{array} \right.$$

Despite the high yields of the desired products and the ease of carrying out the above-mentioned reactions, they cannot be used to obtain aryl(carboranyl)iodonium salts with a given position of the substituent in the aryl ligand since the site of entry of the halonium group is entirely determined by the orienting effect of the substituent in the starting arene. In such cases, use was found for the diazo synthesis of halonium salts [5, 6], which, incidentally, has been the only method available for the preparation of diarylchloronium compounds.

We first demonstrated the applicability of the diazo method for carboranes and thus again illustrated the general nature of this reaction in the synthesis of phenyl-(9-m-carboranyl)chloronium tetrafluoroboride (V), which is the first chloronium salt with a carborane(12) fragment:

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TABLE 1. Aryl-(9-m-carboranyl)halonium Tetrafluoroborides

Compound	Yield, %	Decomp. T, °C	Found/Calc., % C	H	B	Chemical formula	PMR spectrum (100 MHz, ppm from TMS int. stand., in acetone-d_6)
(I)	83	129	21,38 21,26	3,43 3,35	26,01 26,31	$C_8H_{15}B_{11}IF_5$	4,21 s (2H, CH carborane nucl.) 7,28–7,54 m (2H, 3,5-H), 8,16–8,42 m (2H, 2,6-H)
(II)	10(43) [a]	146	20,21 20,06	3,23 3,16	2,75 [b] 2,98	$C_8H_{15}B_{11}IF_4NO_2$	3,45 s (2H, CH carborane nucl.) 7,72–7,96 m (H, 5-H), 8,28–8,76 m (2H, 4,6-H), 8,98 s (H, 2-H) [c]
(III)	84	106	28,12 27,75	4,93 4,66	24,71 24,97	$C_{11}H_{22}B_{11}IF_4$	3,38 s (3H, 4-CH_3), 3,65 s (6H, 2,6-CH_3), 5,22 s (2H, CH carborane nucl.), 8,29 s (2H, arom. H)
(IV)	84	136	22,83 23,29	3,77 3,45	25,47 25,63	$C_9H_{18}B_{11}IF_4O$	3,90 s (3H, OCH_3), 4,18 s (2H, CH carborane nucl.), 7,06–8,16 sym. m (4H, arom. H)
(V)	7 [d]	164	27,69 28,05	4,79 4,71		$C_8H_{16}B_{11}ClF_4$	4,27 s (2H, CH carborane nucl.), 7,78–8,22 m (5H, arom. H)
(VI)	5 [d]	130	26,68 26,65	4,25 4,19	32,38 32,98	$C_8H_{15}B_{11}ClF_5$	4,24 s (2H, CH carborane nucl.), 7,7–8,3 m (4H, arom. H)
(VII)	5 [d]	141	23,61 23,73	3,64 3,73		$C_8H_{15}B_{11}BrF_5$	4,22 s (2H, CH carborane nucl.), 7,5–8,2 m (4H, arom. H)
(VIII)	8 [d]	184	21,23 21,26	3,21 3,35	26,06 26,31	$C_8H_{15}B_{11}IF_5$	4,3 s (2H, CH carborane nucl.), 7,6–8,3 m (4H, arom. H)
(IX)	1,5 [d]	142	26,80 26,65	4,14 4,19	32,46 32,98	$C_8H_{15}B_{11}ClF_5$	4,28 s (2H, CH carborane nucl.), 7,58–7,8 m (2H, 3,5-H), 8,2–8,38 m (2H, 2,6-H)

[a] Relative to iodocarborane consumed.

[b] Analysis for nitrogen.

[c] Spectrum taken in CF_3CO_2H.

[d] The major pathway is the Schieman reaction as shown in our previous work [7].

$$9\text{-}m\text{-}C_2H_2B_{10}H_9Cl \xrightarrow[2)\ HBF_4]{1)\ Ph\overset{+}{N}_2CF_3CO\overline{O}} 9\text{-}m\text{-}C_2H_2B_{10}H_9\overset{+}{Cl}Ph\ \ B\overline{F}_4 \quad (V),\ 7\%$$

3-Fluorophenyl- (VI) and 4-fluorophenyl-(9-m-carboranyl)chloronium tetrafluoroborides (IX) were obtained analogously:

$$9\text{-}m\text{-}C_2H_2B_{10}H_9Cl + Ar\overset{+}{N}_2X^- \xrightarrow{BF_4^-} 9\text{-}m\text{-}C_2H_2B_{10}H_9\overset{+}{Cl}Ar\ \ BF_4^- \ (VI),\ (IX)$$
$$Ar = m\text{-}FC_6H_4,\ X = BF_4\ (VI);\ Ar = p\text{-}FC_6H_4,\ X = CF_3CO_2\ (IX)$$

Finally, the decomposition of aryldiazonium tetrafluoroborides in the presence of iodocarboranes and bromocarboranes led to the corresponding iodonium and bromonium carborane salts:

$$9\text{-}m\text{-}C_2H_2B_{10}H_9X + m\text{-}FC_6H_4\overset{+}{N}_2\ \ BF_4^- \to 9\text{-}m\text{-}C_2H_2B_{10}H_9\overset{+}{X}C_6H_4F\text{-}m\ \ BF_4^-$$
$$X = Br(VII),\ I(VIII). \qquad (VII),\ (VIII)$$

The reactions of aryldiazonium salts with halocarboranes led to a mixture of trifluoroacetic acid and hexafluorobenzene. Upon using hexafluorobenzene as a cosolvent, halocarboranes are completely dissolved upon heating and the reaction mixture becomes homogeneous, resulting in much higher yields of the carboranylhalonium salts. The yields, PMR data, and elemental analysis results are given in Table 1.

EXPERIMENTAL

The PMR spectra of the aryl-(9-m-carboranyl)halonium tetrafluoroborides were taken on a Tesla BS-497 spectrometer. Samples of 9-chloro- and 9-bromo-m-carboranes were obtained by heating bis(9-m-carboranyl)mercury (prepared according to Bregadze [8]) with the corresponding halogen in dichloroethane at reflux. The yield of 9-chloro-m-carborane was 97% after heating for 20 h, while the yield of 9-bromo-m-carborane was 94% after heating for 54%.

1. 4-Fluorophenyl-(9-m-carboranyl)iodonium Tetrafluoroboride (I). A sample of finely ground $K_2S_2O_8$ was added in portions with stirring to a mixture of 70 ml acetic anhydride, 130 ml concentrated sulfuric acid,* 5 g 9-iodo-m-carborane (prepared according to Zakharkin [9]), and 30 ml fluorobenzene at —12°C. The reaction mixture was stirred for 1 h at 0-5°C and then for 6 h at 20°C. The mixture was left overnight and then poured onto 500 g ice. The aqueous solution of the iodonium salt was filtered and the nonsalt products were extracted by benzene and 40 ml 40% HBF_4 was added to the aqueous layer. The precipitated mixture of (I) and KBH_4 was dried and (I) was extracted using nitromethane. After removal of (I) and KBF_4, the filtrate was extracted with 3:1 $MeNO_2$—$CHCl_3$ until a probe of the aqueous layer no longer gave a precipitate upon the addition of aqueous $NaHgBr_3$. The combined organic extracts were evaporated in vacuum to 5-7 ml and (I) was precipitated by the addition of ether. The product was purified by passage through alumina in CH_2Cl_2 and reprecipitation from acetone by the addition of ether. The yield was 6.97 g (83%).

2. 3-Nitrophenyl-(9-m-carboranyl)iodonium Tetrafluoroboride (II). Under the conditions of experiment 1, 4.3 g 9-iodo-m-carborane, 30 ml nitrobenzene, and 12 g $K_2S_2O_8$ in a mixture of 60 ml acetic anhydride and 110 ml conc. sulfuric acid upon stirring for 55 h at 20°C gave (II), which was purified by reprecipitation from nitromethane by the addition of ether. The yield was 0.76 g (10%).

The benzene extract containing the nonsalt products (see experiment 1) was evaporated in vacuum until the solvent was completely removed. The residue, which was a solution of 9-iodo-m-carborane in nitrobenzene, was added dropwise with stirring to a solution of 228 g $SnCl_2 \cdot 2H_2O$ in 228 ml concentrated hydrochloric acid and stirred for 4 h at 70°C with monitoring by thin-layer chromatography. Iodocarborane was extracted by ether from the precipitate formed upon cooling (a mixture of 9-iodo-m-carborane and $(PhNH_3)_2SnCl_6$). The ethereal extracts were evaporated to dryness. The residue in benzene was filtered through silica gel. The removal of benzene in vacuum gave 3.3 g (77% of the amount taken) 9-iodo-m-carborane, mp 110-112°C (from heptane—benzene [9]).

3. Mesityl-(9-m-carboranyl)iodonium Tetrafluoroboride (III). A sample of 1.65 ml concentrated sulfuric acid was added dropwise with stirring to a mixture of 2.9 g 9-m-carboranyliodosobis(trifluoroacetate) (prepared according to our previous procedure [1]), 5.8 ml mesitylene, 6.25 ml acetic anhydride, and 1.45 ml acetic acid cooled to 0°C. The mixture was stirred at 20°C until the oxidizing agent was consumed as indicated by iodine—starch paper and then poured into a cold dilute solution of HBF_4. The precipitate of (III) was filtered off, dried, and reprecipitated from acetone by ether. After removal of (III), the filtrate was extracted by 3:1 $MeNO_2$—$CHCl_3$ and the organic extracts were evaporated in vacuum. An additional amount of (III) was precipitated from the residue by the addition of ether. The overall yield of (III) after purification by passage through alumina in CH_2Cl_2 was 2.35 g (84%).

4. 4-Methoxyphenyl-(9-m-carboranyl)iodonium Tetrafluoroboride (IV). The reaction mixture obtained according to the conditions of experiment 3 from 2.8 g 9-m-carboranyliodosobis(trifluoroacetate), 0.72 ml anisole, 3.1 ml acetic anhydride, 35.8 ml acetic acid, and 0.3 ml concentrated sulfuric acid was poured onto 200 g ice, washed with benzene, treated with 20 ml 40% HBF_4, and extracted with 3:1 $MeNO_2$—$CHCl_3$. The organic extracts were evaporated in vacuum. The addition of ether precipitated (IV) which was purified by reprecipitation from acetone by ether. The yield was 2.2 g (84%).

5. Phenyl-(9-m-carboranyl)chloronium Tetrafluoroboride (V). A solution of 1.82 ml aniline in 8 ml CF_3CO_2H was diazotized at 0°C by the addition of 1.84 g $NaNO_2$. Then, 10.4 g 9-chloro-m-carborane and 35 ml hexafluorobenzene were added with stirring to the solution of phenyldiazonium trifluoroacetate obtained and then 8.3 ml $(CF_3CO)_2O$ was carefully added. The reaction mixture was heated at reflux until the diazonium salt was completely decomposed, as indicated by testing with β-naphthol. The solvents were removed in vacuum. A 2:3 mixture of pentane and ether was added to the residue and the organic layer was repeatedly extracted

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*The mixture should be prepared by the careful dropwise addition of concentrated sulfuric acid to a sample of acetic anhydride cooled to 0°C.

with water. The aqueous extracts were treated with 20 ml 40% HBF_4 and extracted with 3:1 $MeNO_2$–$CHCl_3$. After removal of the solvents in vacuum, (V) was precipitated from the residue by the addition of ether. The product was purified as in experiment 1. The yield was 0.5 g (7%).

6. 3-Fluorophenyl-(9-m-carboranyl)chloronium Tetrafluoroboride (VI). A solution of 4 g 3-fluorophenyldiazonium tetrafluoroboride in 15 ml CF_3CO_2H was added to a solution of 10.9 g 9-chloro-m-carborane in a mixture of 5 ml CF_3CO_2H and 35 ml C_6F_6 heated at reflux. The reaction mixture was heated at reflux for 5 h until the complete decomposition of the diazonium salt. The solvents were evaporated in vacuum. The solid residue was dissolved in acetone and (VI) was precipitated by the addition of ether. The product was purified as in experiment 1. The yield was 0.34 g (5%).

7. 3-Fluorophenyl-(9-m-carboranyl)bromonium Tetrafluoroboride (VII). Under the conditions of experiment 6, 8.4 g 9-bromo-m-carborane, 4 g 3-fluorophenyldiazonium tetrafluoroboride, 20 ml CF_3CO_2H, and 30 ml C_6F_6 upon heating at reflux for 5 h gave (VII), which was purified as in experiment 4. The yield was 0.41 g(5%).

8. 3-Fluorophenyl-(9-m-carboranyl)iodonium Tetrafluoroboride (VIII). Under the conditions of experiment 6, 11.2 g 9-iodo-m-carborane, 4.4 g 3-fluorophenyldiazonium tetrafluoroboride, 25 ml CF_3CO_2H, and 30 ml C_6F_6 upon heating at reflux for 1.5 h gave (VIII), which was purified as in experiment 4. The yield was 0.74 g (8%).

9. 4-Fluorophenyl-(9-m-carboranyl)chloronium Tetrafluoroboride (IX). Under the conditions of experiment 5, 1.9 ml p-fluoroaniline diazotized by 1.84 g $NaNO_2$ in 20 ml CF_3CO_2H and 10.3 g 9-chloro-m-carborane in a mixture of 30 ml C_6F_6 and 9 ml $(CF_3CO)_2O$ upon heating at reflux for 56 h gave (IX), which was purified as in experiment 1. The yield was 0.11 g (1.5%).

CONCLUSIONS

1. 3-Fluorophenyl-, 4-fluorophenyl-, and phenyl-(9-m-carboranyl)chloronium tetrafluoroborides were prepared. These are the first reported carborane chloronium salts.

2. A series of new aryl-(9-m-carboranyl)iodonium and aryl-(9-m-carboranyl)bromonium tetrafluoroborides were obtained with fluoro, nitro, methoxy, and methyl groups in the benzene ring.

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