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THE MERCURATION OF *ortho*- AND *meta*-CARBORANES

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Summary

The mercuration of *ortho*- and *meta*-carboranes is described. This mercuration proceeds at the boron atom of the icosahedral at position 9.

The reaction of direct mercuration of *o*- and *m*-carboranes has not been described until now. We have found that such mercuration did not occur even with boiling of *o*-carborane with mercury acetate for several hours. This may be explained by the electron-deficient properties of the carborane nucleus which hinder electrophilic substitution reactions.

We used a strong mercuration agent, mercury trifluoroacetate [1], to accomplish the mercuration of carborane. The interaction of carborane with one equivalent of mercury trifluoroacetate in trifluoroacetic acid proceeds easily at room temperature with a marked exothermic effect to give the mono-substituted product:

$$m(o)\text{-}CHB_{10}H_{10}CH + (CF_3CO_2)_2Hg \rightarrow CF_3CO_2Hg\text{-}m(o)\text{-}CHB_{10}H_9CH$$

o-Carborane reacts much faster than *m*-carborane. This fact confirms the conclusion that *o*-carborane is attacked by electrophilic agents to a greater extent than *m*-carborane [2]. Treatment of carboranyltrifluoroacetates in acetone with an aqueous solution of sodium chloride has led to the corresponding chlorides:

$$CF_3CO_2Hg\text{-}m(o)\text{-}CHB_{10}H_9CH \xrightarrow{NaCl} ClHg\text{-}m(o)\text{-}CHB_{10}H_9CH$$

The substitution of *o*- and *m*-carboranes proceeds at position 9 of the carborane nucleus. The position of substitution was determined by bromination of carboranylmercury chlorides in carbon tetrachloride to give the known bromides:

$$9\text{-}ClHg\text{-}m(o)\text{-}CHB_{10}H_9CH \xrightarrow{Br_2} 9\text{-}Br\text{-}m(c)\text{-}CHB_{10}H_9CH$$

Table 1 contains physical data of the compounds obtained.

TABLE 1

BORON-SUBSTITUTED CARBORANYLMERCURY COMPOUNDS

Compounds	M.p. (°C)	Yield (%)	Analysis Found (calcd.) (%)					m/e
			C	H	B	Cl	Hg	
9-CF_3CO_2Hg-*o*-$HCB_{10}H_9CH$	160—162 [a]	66	10.42 (10.51)	2,32 (2,42)	22,91 (23,67)		43.38 (43.90)	
9-CF_3CO_2Hg-*m*-$HCB_{10}H_9CH$	117—118 [a]	71	10.31 (10.51)	2,54 (2,42)	23,08 (23,67)		(43.90)	
9-ClHg-*o*-$HCB_{10}H_9CH$	263—264 [b]	90	7.08 (6.33)	2,99 (2,92)	28,47 (28,52)	9,26 (9,34)	52.01 (52,87)	379
9-ClHg-*m*-$HCB_{10}H_9CH$	266—267 [b]	92	6.67 (6.33)	2.94 (2,92)	28.20 (28,52)	9,53 (9,34)	52.40 (52.87)	379

[a] Crystallized from toluene/hexane. [b] Crystallized from toluene.

References

1 H.C. Brown and R.A. Wirkkala, J. Amer. Chem. Soc., 88 (1966) 1447.
2 R.N. Grimes, Carboranes, Academic Press, New York/London, 1970, p. 173.