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

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Summary

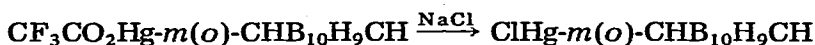
The mercuration of *ortho*- and *meta*-carboranes is described. This mercuration proceeds at the boron atom of the icosahedral at position 9.

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:



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:



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:

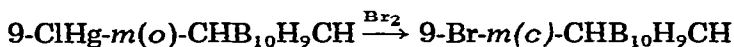


Table 1 contains physical data of the compounds obtained.

TABLE I
BORON-SUBSTITUTED CARBORANYLMERCURY COMPOUNDS

Compounds	M.p. (°C)	Yield (%)	Analysis Found (calcd.) (%)					m/e
			C	H	B	Cl	Hg	
9-CF ₃ CO ₂ Hg-o-HCB ₁₀ H ₉ CH	160-162 ^a	66	10.42 (10.51)	2.32 (2.42)	22.91 (23.67)			43.38 (43.90)
9-CF ₃ CO ₂ Hg-m-HCB ₁₀ H ₉ CH	117-118 ^a	71	10.31 (10.51)	2.64 (2.42)	23.08 (23.67)			(43.90)
9-ClHg-o-HCB ₁₀ H ₉ CH	263-264 ^b	90	7.08 (6.33)	2.99 (2.92)	28.47 (28.52)	9.26 (9.34)		52.01 (52.87)
9-ClHg-m-HCB ₁₀ H ₉ CH	265-267 ^b	92	6.67 (6.33)	2.94 (2.92)	28.20 (28.52)	9.53 (9.34)		52.40 (52.87)

^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.