

Preliminary communication

CYANOETHYLATION OF CARBORANES

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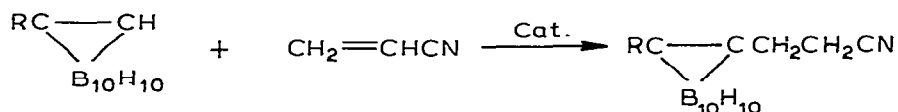
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Summary

The methine group of *o*-carboranes react with acrylonitrile and alkali catalyst to form β -cyanoethylcarboranes.

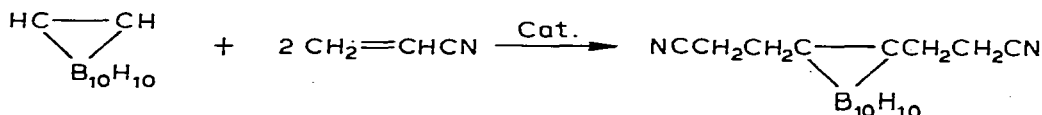
The highly mobile hydrogen atoms of methine groups of carboranes may be substituted by metals under the action of metallizing agents [1]. *C*-Metal carborane derivatives were used to synthesize various types of compounds containing carborane nuclei [1]. However, only one reaction is employed for attaching functional groups to carbon atoms in carboranes, viz. direct *C*-mercuration of *o*-carboranes by organomercury hydroxides [2], which directly based the acidic nature of the hydrogen atoms.

We have found that *o*-carborane and its *C*-alkyl, -alkenyl and -aryl derivatives readily undergo cyanoethylation when exposed to acrylonitrile and an alkali catalyst:



(R = H, CH₃, C₆H₅, CH₂=C(CH₃))

o-Carborane itself contains two active hydrogen atoms and it can easily be converted into the bis(cyanoethyl) derivative.



Cyanoethylation of carboranes is the first example of addition to α,β -unsaturated compounds involving the C—H bond of carboranes. This reaction obeys the general rules of cyanoethylation of compounds with mobile hydrogen atoms.

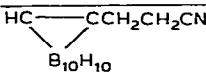
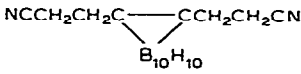
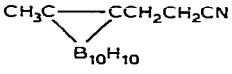
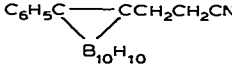
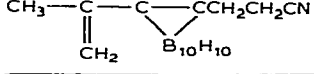
The alkali catalysts used were hydroxides and alcoholates of alkali metals, and quaternary ammonium bases. The best results were obtained with triton-B (40% aqueous trimethylbenzylammonium hydroxide) as catalyst. The reaction was carried out in dioxane, tetrahydrofuran, pyridine and acetonitrile.

General experimental technique of cyanoethylation of carboranes

To 50 ml of a 0.05 M solution of *o*-carborane or its *C*-monosubstituted derivative in one of the above solvents was added 1 ml 40% aqueous triton-B

TABLE 1

THE CONSTANTS AND THE ELEMENTAL COMPOSITION OF *o*-CYANOETHYL *O*-CARBORANES

Compound	M.p. (°C)	Analysis (Found (calcd.) (%))				Formula
		C	H	B	N	
	138—139	31.8 (30.47)	7.46 (7.61)	54.55 (54.82)	7.11 (7.11)	C ₅ H ₁₅ B ₁₀ N
	220—222				10.88 (11.20)	C ₈ H ₁₈ B ₁₀ N ₂
	163—164	33.91 (34.12)	8.07 (8.06)	50.88 (51.18)	6.71 (6.64)	C ₆ H ₁₇ B ₁₀ N
	182—183	48.47 (48.36)	7.11 (6.96)	39.42 (39.56)	5.08 (5.13)	C ₁₁ H ₁₉ B ₁₀ N
	114—115	40.57 (40.51)	7.76 (8.02)	45.44 (45.57)	5.92 (5.91)	C ₈ H ₁₉ B ₁₀ N

and then 0.06 M acrylonitrile. The mixture was allowed to stay at room temperature for 2 h and then poured into water. The precipitate was filtered, washed with water, dried over P₂O₅ in a desiccator and crystallized from a heptane/dichloroethane mixture. The yield of cyanoethylation products was 70—95%. The elemental analyses of the compounds obtained are presented in Table 1.

References

- 1 L. Grimes, *Carboranes*, Mir, Moscow, 1974.
- 2 L.I. Zakharkin, V.N. Kalinin and L.S. Podvisotskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1968) 688.
- 3 A.P. Terentyev and A.N. Kost, *Reaktsii i Metody Issledovaniya Organicheskikh Soedineniy*, 2 (1952) 47.