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SYNTHESIS OF 2- AND 4-ARYL-*m*-CARBORANES AND ELECTRONIC EFFECTS OF THE 4-*m*-CARBORANYL GROUP *

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Summary

Gas-phase isomerization of 3-aryl-*o*-carboranes under vacuum in a flow at 550–600°C leads to the formation of equal amounts of 2- and 4-aryl-*m*-carboranes which are easily separated by column chromatography. Determination of ionization constants of 4-(*p*- and *m*-carboxyphenyl)-*m*-carboranes and measurement of ¹⁹F chemical shifts in NMR spectra of 4-(*p*- and *m*-fluorophenyl)-*m*-carboranes have shown that the 4-*m*-carboranyl group as a substituent displays electron properties similar to those of a hydrogen atom

Introduction

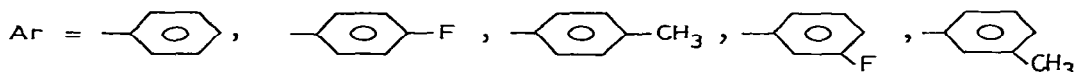
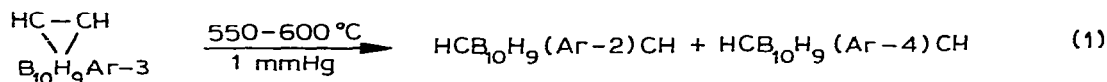
At present, only a few members of a series of *B*-arylcaboranes are known 1,2-Dicarbollide [2–7] and 1,7-dicarbollide [8] ions with arylboron dihalide give 3-aryl-*o*- and 2-aryl-*m*-carboranes 3-, 4-, and in certain cases 9-aryl-*o*-carboranes [9,11] were synthesized by the interaction of dianions of dicarbododecacarborates [14] with arylmagnesium halide followed by the oxidation of *B*-aryl dianions. The general method of preparation of 2- and 4-substituted *m*-carboranes by gas-thermal isomerization of 3-substituted *o*-carboranes under vacuum in the flow was developed by us earlier [12,13]. The present paper discusses isomerization of 3-aryl-*o*-carboranes into *B*-aryl-*m*-carboranes on the basis of the method mentioned above.

Discussion

B-Arylcaboranes constitute an interesting class of compounds which enable quantitative assessment of the electronic effects of carboranyl groups. We found that 3-aryl-*o*-carboranes, when passed through a quartz tube at 550–600°C

* Preliminary communication see ref 1

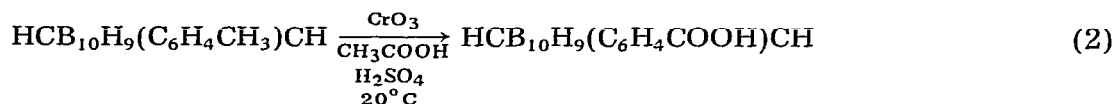
under vacuum, easily isomerize into 2- and 4-substituted *m*-carboranes in approximately equal amounts (eq 1) Total yield of *B*-aryl-*m*-carboranes is high The



formation of 2-aryl-*m*-carboranes was proven by comparing their properties with those of authentic samples obtained earlier [8], the structure of 4-aryl-*m*-carboranes was determined by X-ray analysis * The isomers were separated on silica gel and alumina columns using hexane as eluting solvent

The method developed for the preparation of 4-aryl-*m*-carboranes made it possible to evaluate quantitatively the electronic effects due to the 4-*m*-carboranyl group Data [12,13] on ionization constants of 4-oxy-, amino-, and carboxy-*m*-carboranes offer a means of only qualitative assessment of the electronic characteristics of the 4-*m*-carboranyl group

Oxidation of 4-(*p*- and *m*-tolyl)-*m*-carboranes with chromium anhydride in acetic acid by the published procedure [4,5] yields 4-(*p*- and *m*-carboxyphenyl)-*m*-carboranes (eq. 2)



Ionization constants of 4-(*p*- and *m*-carboxyphenyl)-*m*-carboranes in 75% ethanol were determined and the Hammett constants σ_p and σ_m for the 4-*m*-carboranyl group were calculated (Table 1) The Hammett constants for the 2-*m*-carboranyl group known from the literature [8] are given for comparison It is seen from Table 1 that the 4-*m*-carboranyl group, unlike the 2-*m*-carboranyl group which is an electron-accepting substituent, possesses neither electron-donating nor electron-accepting properties This phenomenon can be attributed to the distribution of electron density over the *m*-carborane nucleus [4] Weak electron-accepting properties of the 2-*m*-carboranyl group are explained by the presence of the partial positive charge (+0.09) on the boron atom B(2), while a practical absence of the charge (+0.02) on B(4) atom explains the fact that the 4-*m*-carboranyl group possesses neither electron-accepting nor electron-donating properties The similarity of the constants σ_p and σ_m allows us to conclude that the 4-*m*-carboranyl group will display an inductive effect

Taft's method based on the measurement of ^{19}F chemical shifts in the NMR spectra of fluorophenylcarboranes, proved greatly informative for the carborane series. This method has been applied successfully to the evaluation of electronic effects of 1-*o*- [6,16], 1-*m*- [6,16], 1-*p*- [17], 3-*o*- [6,7], 4-*o*- [10,11], 9-*o*- [10,11], and 2-*m*- [8] carboranyl groups NMR spectra [19] of 4-(*p*- and *m*-fluorophenyl)-*m*-carboranes in a number of solvents were taken

* Data on X-ray analysis of 4-aryl-*m*-carboranes will be given in a separate communication

TABLE 1

APPARENT IONIZATION CONSTANTS OF SUBSTITUTED BENZOIC ACIDS ($\text{RC}_6\text{H}_4\text{COOH}$) IN 75% ETHANOL AND HAMMETT s CONSTANTS σ_p AND σ_m FOR R GROUPS

Substituent R	$\text{p}K_a$	Hammett s constant
<i>p</i> (4- <i>m</i> -Carboranyl)-	6.53	0.02
<i>m</i> (4- <i>m</i> -Carboranyl)-	6.66	-0.02
H	6.58	0
<i>p</i> (2- <i>m</i> -Carboranyl)- [8]	5.32	0.15
<i>m</i> (2- <i>m</i> -Carboranyl)- [8]	6.34	0.14

and inductive and resonance constants were calculated for the 4-*m*-carboranyl group (Table 2). The inductive constant of the 4-*m*-carboranyl group, like the Hammett constant, is close to zero.

As distinct from ^{19}F chemical shifts in NMR spectra of 4-fluorophenyl-*o*-carboranes [10,11], clear shift-solvent dependence in 4-fluorophenyl-*m*-carboranes was not observed even though the *m*-carborane molecule is able to form hydrogen bonds with aprotic solvents [6,18]. This may be due to the fact that the hydrogen bond formation energy is lower for *m*-carboranes than for *o*-carboranes and, as a result, the influence of this bond on shielding the fluorine atom in the benzene ring is insignificant.

It is interesting to note that the electronic effect due to the 4-*o*-carboranyl group ($\sigma_p = \sim 0.05$, $\sigma_m = -0.03$, $\sigma_i = -0.04$) is close to that of the 4-*m*-carboranyl group (the present paper). The 4 positions in the *m*-carborane (6, 8, 11) and *o*-carborane molecules (5, 7, 11) are equatorial and, according to calculated data [14], serve as a boundary between oppositely charged skeleton atoms of an icosahedron. Positions 1,2 (C atoms), 3,6 (B atoms) in *o*-carborane and positions 1,7 (C atoms), 2,3 (B atoms) in *m*-carborane carry a partial positive charge, and carboranyl groups linked through these atoms display an electron-accepting effect. Partial negative charges are concentrated on boron atoms in positions 8, 9, 10, 12 of *o*-carborane and in positions 5, 9, 10, 12 of *m*-carborane and therefore one should expect that carboranyl groups will display an electron-donating effect. The latter has been experimentally confirmed by the investigation of the electronic effect of the 9-*o*-carboranyl group [10].

TABLE 2

CHEMICAL SHIFTS δ OF ^{19}F NUCLEI IN THE NMR SPECTRUM OF 4-FLUORENYL-*m* CARBORANE AND CALCULATED σ CONSTANTS FOR THE 4-*m* CARBORANYL GROUP

Solvent	δ_p^{F}	δ_m^{F}	σ_i	σ_R^0
CCl_4	0.15	0.90	-0.04	0.02
Dioxane	0.55	0.90	-0.04	0.01
THF	0.7	0.6	0	0
Hexametapol	1.1	0.83	-0.03	-0.01

^a ppm relative to fluorobenzene

TABLE 3
MELTING POINTS, ¹H NMR SPECTRA IN CCl₄ AND ELEMENTAL ANALYSIS OF THE COMPOUNDS OBTAINED

Compound	T _m (°C)	Found (%)			Formula	Calculated (%)			¹ H NMR spectra ^a
		C	H	B		C	H	B	
4 Phenyl <i>m</i> carborane 1 (<i>p</i> Toly)- <i>m</i> carbo rane	36.5-37 61-62	43.69 46.18	7.34 7.70	48.65 46.12	C ₈ H ₁₆ B ₁₀ C ₉ H ₁₈ B ₁₀	43.61 46.13	7.32 7.74	49.06 46.13	3.0 (CH(2)), 7.35 (C ₆ H ₅ (5)), 2.3 (CH ₃ (3)), 2.92 (CH(2)), 7.30 (C ₆ H ₄ (4))
4 (<i>m</i> -Toly)- <i>m</i> carbo rane	50-52	46.10	7.78	45.93					2.3 (CH ₃ (3)), 2.90 (CH(2)), 7.30 (C ₆ H ₄ (4))
4 (<i>p</i> Fluorophenyl) <i>m</i> carborane	56-56.5	40.45	6.31	45.41	C ₈ H ₁₅ B ₁₀ F	40.4	6.35	45.4	3.1 (CH(2)), 7.35 (C ₆ H ₄ (4)) 3.1 (CH(2)), 7.30 (C ₆ H ₄ (4))
4 (<i>m</i> Fluorophenyl) <i>m</i> carborane, ^β				45.44					
4 (<i>p</i> Carboxyphenyl) <i>m</i> carborane	200-201	40.73	6.15	40.73					
4 (<i>m</i> Carboxyphenyl) carborane	234-235	40.87	6.01	40.54	C ₉ H ₁₆ B ₁₀ O ₂	40.89	6.10	40.90	

^a Chemical shifts are given in ppm relative to tetramethylsilane used as an internal standard. Assignment and relative integral intensity of the signal are given in parentheses. ^β Boiling point 150-152°C/2 mmHg

Experimental

The purity of initial compounds and products was controlled by gas-liquid chromatography on a "Tsvet-4" chromatograph at 230–250°C, columns (2 m, I D 4 mm) being filled with celite-425 treated with 15% silicone-301. Column and thin-layer chromatography was performed on neutral alumina, 100–160 μm silica gel and on plates with fixed layer of "Silufol" silica gel. Measurements of pH were made on LPU-01 pH meter with a glass electrode. A silver chloride electrode was used as a reference. Titration and calculation followed the published procedure [19]. Measurement of ^{19}F chemical shifts in NMR spectra was conducted as in the literature [6].

General procedure for the gas phase thermal isomerization of 3-aryl-o-carboranes in vacuum

3-Aryl-*o*-carborane was evaporated under 1 mmHg vacuum and the vapours passed through a quartz tube ($d = 20$ mm, $l = 0.5$ m) heated to 580–600°C. A mixture of 2- and 4-aryl-*m*-carboranes was obtained in 80–90% yield. The isomers were separated by column chromatography on silica gel using hexane as the eluting solvent.

Melting points, parameters of ^1H NMR spectra taken in CCl_4 and results of elemental analysis of the compounds obtained are presented in Table 3.

Oxidation of 4-tolyl-m-carborane

To a solution of 1 g of 4-tolyl-*m*-carborane in a mixture of 60 ml of CH_3COOH , 15 ml of $(\text{CH}_3\text{CO})_2\text{O}$ and 3 ml of concentrated H_2SO_4 at 20–25°C was added gradually 6 g of CrO_3 with stirring. After 2 h the reaction mixture was poured into 0.5 l of cold water. The precipitate formed was filtered off and dried over P_2O_5 . The acid was sublimated under vacuum and recrystallized from an ethanol-water mixture to give a yield of 65%.

Melting points and results of elemental analysis of the acids obtained are given in Table 3.

References

- 1 V N Kalinin, N I Kobel'kova and L I Zakharkin, *Zh Org Khim*, 48 (1978) 938
- 2 M F Hawthorne and P A Wegner, *J Amer Chem Soc*, 90 (1968) 896
- 3 M F Hawthorne and P A Wegner, *J Amer Chem Soc*, 87 (1965) 4392
- 4 L I Zakharkin, V N Kalinin and I P Shepilov, *Izv Akad Nauk SSSR Ser Khim*, (1966) 1286
- 5 L I Zakharkin, V N Kalinin and I P Shepilov, *Dokl Akad Nauk SSSR*, 174 (1967) 606
- 6 L I Zakharkin, V N Kalinin, A P Snyakin and B A Kvasov, *J Organometal Chem*, 18 (1969) 19
- 7 R G Adler and M F Hawthorne, *J Amer Chem Soc*, 92 (1970) 6174
- 8 L I Zakharkin and V N Kalinin, *Zh Org Khim*, 43 (1973) 853
- 9 V N Kalinin, N I Kobel'kova and L I Zakharkin, *Zh Org Khim*, 47 (1977) 963
- 10 V N Kalinin, N I Kobel'kova, A V Astakhin and L I Zakharkin, *Izv Akad Nauk SSSR*, (1977) 2376
- 11 V N Kalinin, N I Kobel'kova, A V Astakhin, A I Gusev and L I Zakharkin, *J Organometal Chem*, 149 (1978) 9
- 12 L I Zakharkin, V N Kalinin and E G Rys, *Synth React Inorg Met-Org Chem*, 5 (1975) 257
- 13 L I Zakharkin, V N Kalinin and N I Kobel'kova, *Synth React Inorg Met-Org Chem*, 6 (1976) 91
- 14 F Thomas, W Koetzle and W N Lipscomb, *Inorg Chem*, 9 (1970) 2743
- 15 R W Taft, E Price, I R Fox, J C Lewis, K K Andersen and J T Davis, *J Amer Chem Soc*, 85 (1963) 3146
- 16 M F Hawthorne, T E Berry and P A Wegner, *J Amer Chem Soc*, 87 (1965) 4746
- 17 L I Zakharkin, V N Kalinin and E G Rys, *Izv Akad Nauk SSSR Ser Khim*, (1974) 2632
- 18 L E Vinogradova, L A Leytes, V N Kalinin and L I Zakharkin, *Izv Akad Nauk SSSR Ser Khim*, (1969) 2847
- 19 A Albert and E P Sergeant, *Ionization Constants of Acids and Bases*, Wiley, New York, 1962