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ALKYLATION OF AROMATIC HYDROCARBONS BY 1-FLUOROMETHYL-0,m-CARBORANES BY THE ACTION OF A1C1,

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In our previous work [1], we showed that 1-chloromethyl- and 1-bromomethyl-o-carboranes, in contrast to 1-(β -chloroethyl)- and 1-(β -chloropropyl)-o-carboranes, do not alkylate benzene in the presence of AlCl₃ upon prolonged heating. The reactivity of primary alkyl halides in the alkylation of benzene in the Friedel-Crafts reaction increases in the series RI < RBr < RCl < RF [2]. In this regard, we studied the alkylation of aromatic hydrocarbons by 1-fluoromethyl-o-carborane (I) and found that, in contrast to 1-chloromethyl-o-carborane, it alkylates benzene, toluene and p-xylene in the presence of AlCl₃.

 $\begin{array}{c} \text{HC-CCH}_2\text{F} + \text{ArH} \xrightarrow[\text{AlCl}_3]{} \text{HC-CCH}_2\text{Ar} + \text{HC-CCH}_2\text{Cl} \\ \overbrace{\text{B}_{10}\text{H}_{10}}^{\text{HC}} \stackrel{i}{\underset{\text{B}_{10}\text{H}_{10}}{}} \stackrel{i}{\underset{\text{B}_{10}\text{H}_{10}}{}} \\ (1) \quad (1\text{Va-c}) \\ \text{ArH} = \text{C}_6\text{H}_6 (a); \text{ PhMe (b); } p\text{-MeC}_6\text{H}_4\text{Me (c)}. \end{array}$

The reaction proceeds at 60°C. In addition to 1-arylmethyl-o-carboranes (IVa)-(IVc), some amount of 1-chloromethyl-o-carborane is formed due to the exchange reaction between (I) and $AlCl_3$ which does not react with aromatic hydrocarbons. 1-Fluoromethyl-m-carborane (II) also alkylates benzene by the action of $AlCl_3$.

 $\begin{array}{c} m\text{-HCB}_{10}\text{H}_{10}\text{CCH}_2\text{F} + \text{C}_6\text{H}_6 \xrightarrow{\text{AlCI}_3} m\text{-HCB}_{10}\text{H}_{10}\text{CCH}_2\text{Ph} \\ (\text{II}) & (\text{V}) \end{array}$

Thus, in the series of 1-halomethyl-o,m-carboranes, the rather highly polarized $RCH_2F...AlCl_3$ capable of the electrophilic alkylation of aromatic hydrocarbons is formed only in the case of 1-fluoromethyl-o,m-carborane due to the high polarity of the C-F bond.

Carborane (I) was synthesized in our previous work from 1-hydroxymethyl-o-carborane (III) and SF₄ [3]. In the present work, we attempted to obtain (I) by the reaction of (III) with α -fluoroalkylamines which are commonly used for the substitution of the hydroxyl group by fluorine [4]. However, the following transformations proceed in this case:



The reaction of bis(hydroxymethyl)-o-carborane with the Yarovenko reagent leads to the formation of 3,4-carborano-2,5-tetrahydrofuran (VII) [15].

Carborane (II) was obtained in our previous work in low yield [3]. We have found that (II) is formed in high yield upon passing (I) through a quartz tube in vacuum:

$$\begin{array}{c} HC-C-CH_2X \xrightarrow{450'} m\text{-}HCB_{10}H_{10}CCH_2X \\ \searrow \\ H_{10}H_{10} \\ (I), (VIII) \\ X = F(I), (II); OAc(VIII), (IX). \end{array}$$

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Similarly, 1-acetoxymethyl-o-carborane (VIII) is readily isomerized to the m-isomer (IX).

EXPERIMENTAL

The ¹H and ¹⁹F NMR spectra were taken on a Bruker WP-200SY spectrometer in CC1₄ with HMDS as the internal standard and CF_3CO_2H as the external standard. The IR spectra were taken neat on a UR-20 spectrometer.

General	Proce	edure	for	the	Alkylatic	on j	of	Aromatic
Hydrocan	rbons	by 1	-Fluc	orome	ethyl-o,m	Ca	rbo	oranes
(I) and	(II)							

A sample of 5 mmoles $AlCl_3$ was added to 5 mmoles (I) or (II) in 5 ml aromatic compound, heated for 1 h at 50-60°C and cooled. Dilute hydrochloric acid was added. The organic layer was separated and dried over $CaCl_2$. The aromatic hydrocarbons were removed in vacuum and the residue yielded (IVa)-(IVc), of which (IVa) and (IVb) were identified with authentic samples [6, 7].

1-(2,4-Dimethylphenyl)methyl-o-carborane (IVc) was obtained in 25% yield, mp 65-68°C (hexane). PMR spectrum (δ , ppm): 2.03 s (6H), 2.29 s (2H), 3.42 s (1H), 6.95 m (3H). Found: C, 50.16; H, 8.19%. Calculated for $C_{11}H_{22}B_{10}$; C, 50.34; H, 8.39%.

a) 1-Benzyl-m-carborane (V) was obtained in 75% yield identical to the sample obtained by method b.

b) A sample of 20 mmoles BuLi in 13.2 ml benzene was added to a solution of 20 mmoles m-carborane in 20 ml ether and heated at reflux for 1 h. Then, 20 mmoles PhCH₂Cl in 20 ml ether was added dropwise and the mixture was heated at reflux for 3 h. The reaction mixture was diluted with 10 ml water. The organic layer was separated and dried over CaCl₂. The solvent was evaporated and then 0.7-g m-carborane was sublimed initially in vacuum. Distillation in vacuum gave 1.4 g (42%) (V), bp 150-153°C, n_D^{20} 1.6788. PMR spectrum (δ , ppm): 2.55 s (1H), 3.05 s (2H), 7.1-6.9 m (5H). Found: C, 46.05; H, 7.48%. Calculated for C₉H₁₈B₁₀: C, 46.12; H, 7.67%.

 $\frac{1-Fluoromethyl-m-carborane (II)}{550°C at 10 mm Hg to give 4 mmoles (80%) (II), mp 178-180°C. ¹⁹F NMR spectrum (<math>\delta$, ppm): 119.2 t (CH₂F), J_{HF} = 48 Hz. Found: C, 20.56; H, 7.36; F, 9.69%. Calculated for C₃H₁₃B₁₀F: C, 20.45; H, 7.39; F, 10.78%.

<u>1-Acetoxy-m-carborane (IX).</u> By analogy to the preceding procedure, 10 mmoles (VIII) at 550°C and 15 mm Hg gave 5 mmoles (50%) (IX), mp 103-107°C. Found: C, 28.65; H, 7.34%. Calculated for $C_5H_{16}B_{10}O_2$: C, 27.75; H, 7.40%.

<u>o-Carboranylmethyl</u> Formate (VI). A solution of 8 mmoles (III) in 20 ml abs. ether was added to 16 mmoles Me_2NCHF_2 and maintained for 8 h at 20°C in an argon stream. Ether was evaporated. The residue was washed with 10 ml 20% aq. NaHCO₃. The organic layer was separated and dried over CaCl₂ to give 1.4 g of a viscous yellow oil, which was extracted with hot heptane. Heptane was evaporated. The residue was crystallized. Sublimation gave 0.8 g (60%) (VI), mp 41-42°C. IR spectrum (ν , cm⁻¹): 1730 (C=O), 2620 (BH), 3080 (CH). PMR spectrum (δ , ppm): 4.6 s (2H), 7.97 s (1H). Found: C, 24.14; H, 6.92; B, 53.41%. Calculated for C₄H₁₄B₁₀O₂: C, 23.74; H, 7.16; B, 53.41%.

<u>3,4-Carborano-2,5-tetrahydrofuran (VII)</u>. A sample of 10 mmoles bis(hydroxymethyl)-ocarborane and 12 mmoles 1,2-trifluoro-2-chloroethyldiethylamine were mixed and maintained for 1 h at 30°C. Distillation of the reaction mixture in vacuum gave a colorless oil and the crystalline residue was recrystallized from ethanol to give 7 mmoles (VIII) (70%), mp 259°C [5].

CONCLUSIONS

l-Fluoromethyl-o,m-carboranes undergo the Friedel-Crafts reaction with aromatic hydrocarbons in the presence of $AlCl_3$.

*This experiment was carried out jointly with K. M. Uyzbaev and M. G. Meiramov.

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NUCLEAR QUADRUPOLE RESONANCE IN MSbClF₃ COMPOUNDS

 $(M = Na, K, Cs, NH_4)$

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Interest in the dynamics of the motion of the crystal lattices of Sb(III) fluorinecontaining complexes is a function of the various electrophysical and phase transitions discovered for these compounds. In our previous work [1, 2], we carried out an NQR study of MSbF₄ compounds (M = Na, K, NH₄ and CN_3H_6) in a broad temperature range. In the present communication, results are given for a study of the temperature dependence of the NQR parameter for MSbClF₃ complexes (M = Na, K, Cs and NH₄). The ^{121,123}Sb NQR spectra of these compounds obtained at 77°K were discussed in our previous work [3].

EXPERIMENTAL

Samples of MSbClF₃ (M = Na, K, Cs and NH₄) were prepared from aqueous solutions according to our previous procedure [4]. The ¹²³Sb NQR spectra at from 77 to 390°K were taken on an ISSh-2-13 spectrometer with a temperature-control device. Figure 1 shows the change in the quadrupole interaction constants (e²Qq, MHz) and asymmetry (η , %) of the electric field gradient (EFG) of the antimony atoms found from the experimental data using the absorption frequencies of two ¹²³Sb transitions (+1/2 \neq +3/2 and +3/2 \neq +5/2).

RESULTS AND DISCUSSION

<u>NaSbClF₃'H₂O</u>. All the fluoride ions in the structure of NaSbClF₃'H₂O [5] are terminal (Sb-F, 193-2.01 Å), while each chloride ion is bound to four antimony ions (Sb-Cl, 2.83, 3.00, 3.42 and 3.55 Å). Due to bridging chloride atoms, the antimony polyhedra form (SbEF₃Cl)ⁿ_n layers. Formally limiting the coordination spheres of the atoms in NaSbF₄ [6] and NaSbClF₃' H₂O [5] to the five nearest ligands, we may draw some analogy in their structural patterns consisting of infinite zigzag chains formed by distorted SbEX₅ octahedra attached by common apices.

According to the ^{121,123}Sb NQR spectra [3], the structure of NaSbClF₃'H₂O at 77°K, like the structure of NaSbF₄, contains crystallographically equivalent antimony atoms but with higher local symmetry of the environment of the resonance atoms. Figure la shows the temperature dependence of e^2Qq and $\eta^{123}Sb$ for NaSbClF₃'H₂O. The NQR spectrum at 77-289°K is a singlet with a steady decrease in the NQR frequency as in the case of NaSbF₄ [1]. The relative NQR frequency intensity for NaSbClF₃'H₂O gradually falls and signals are not observed above 289°K, which is apparently a result of greater internal motion. The smooth decrease in the NQR indices with increasing temperature indicates the lack of structural phase transitions in NaSbClF₃'H₂O at 77-289°K. These results are in accord with the Bayer-Kushida theory [7], which states that the major reason for the change in the NQR frequency of a quadrupole

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