SYNTHESIS OF 9-(FLUOROPHENYL)-o-, 9-(FLUOROPHENYL)-m-, AND 2-(FLUOROPHENYL)p-CARBORANES AND DETERMINATION OF ELECTRONIC EFFECTS OF 9-o-, 9-m-, AND 2-p-CARBORANYL GROUPS

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A dependence of the electronic effects of the carboranyl groups on the position of the substituent is characteristic for carborane systems. The electronic effects of the 1-o-, 3-o-, 4-o-, 9-o-, 1-m-, 2-m-, 4-m-, 9-m-, 1-p-, and 2-p-carboranyl groups have been determined at the present time [1-4]. A study of the 9-o-, 9-m-, and 2-p-carboranyl groups by various methods [3, 4] led to respective values for the induction effects of the 9-o- and 9-m-carboranyl groups of $\sigma_i = -0.23$ and -0.34, which contradicts the data given in [4-6] regarding the greater value of the electron-donor effect of the 9-o- when compared with the 9-m-carboranyl group.

The Taft method gives good results when determining the electronic effects of the o-, m-, and p-carboranyl groups that contain a substituent on both the C atom and the B atoms of the carborane rings [1, 2, 7].

We successfully used the previously developed [8] method of adding organic groups to the B atoms of the o-, m-, and p-carboranes to synthesize the 9-(fluorophenyl)-o-, 9-(fluorophenyl)-m-, and 2-(fluorophenyl)-p-carboranes. This made it possible to determine the electronic effects of the 9-o-, 9-m-, and 2-p-carboranyl groups within the framework of the Taft method alone. The 9-(fluorophenyl)-o-(I), (II), and m-carboranes (III), (IV) are smoothly formed by heating for 30 h the 9-iodo-o- and 9-iodo-m-carboranes with the m- and p-fluorophenylmagnesium bromides in the presence of catalytic amounts of $(Ph_3P)_2PdCl_2$.

o,m-HCB₁₀H₉(9-I)CH + m,p-FC₆H₄MgBr $\xrightarrow{\text{EtaO}}$ $\longrightarrow o,m$ -HCB₁₀H₉-9-(m,p-C₆H₄F)CH (I)-(IV)

The analogous reaction of 2-iodo-p-carborane with fluorophenylmagnesium bromides is much slower and requires 60 h of heating for completion.

Company	Yield,		Found/Calc.,%			Empirical	
Compound	%	mp, C	С	H	В	formula	
HC-CH]		
BtoHs-9-m-C6H4F	(I)	63	132-134 (hexane)	$\frac{40,33}{40,32}$	$\frac{6,22}{6,34}$	$\frac{45,34}{45,30}$	$C_8H_{15}B_{10}F$
нс-сн		70	9697	40,07	6,44	45,23	$\mathrm{C_8H_{15}B_{10}F}$
B10H9-9-p-C6H4F m-HCB10H9-9-(m-C6H4F)CH	(11) (111)	70	(nexane) 89-91	40,32	6,34 5,98	45,30 45,61	$C_8H_{15}B_{10}F$
m-HCB10Ha-9-(n-CoH4E)CH	(IV)	76	(hexane) 58-59	40,32	6,34	45,30	C.H.B.oF
··· I optime o (P optime) off	(2.1.)		(hexane)	40,32	6,34	45,30	0.011132101
p-HCB10H9-2-(m-C6H4F)CH	(V)	68	bp,120° (1 mm)	40,41	6,31	44,84	$C_8H_{15}B_{10}F$
p-HCB10H+-2-(p-C6H4F)CH	(VI)	79	5051	40,33	6,31	44,83	$C_8H_{15}B_{10}F$
		1	(pentane)	40,32	6,34	45,30	

TABLE 1. Elemental Analysis Data and Constants of Substituted pand m-Fluorophenyl-9-o-, 9-m-, and 2-p-carboranes

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Solvent	HCCH \searrow $B_{10}H_3-9-(m, p-C_6H_4F)$			m	-HCB ₁₀ H ₉ 9-(7	n,p-C ₆ H₄F)CI	I	$p ext{-} ext{HCB}_{10} ext{H}_{2} ext{-}2(m,p ext{-} ext{C}_{0} ext{H}_{4} ext{F}) ext{CH}$				
	$\delta_p^{\mathbf{F}}$	δ_m^F	σΙ	σ_R°	$\delta_p^{\mathbf{F}}$	$\delta_m^{\mathbf{F}}$	σ _I	σ_R°	$\delta_p^{\mathbf{F}}$	δ ^F _m	σι	σ_R°
CCl ₄ CHCl ₃ THF	$^{+2.59}_{+2.23}_{+3.34}$	+1,76 +1,53 +2,07	-0,16 -0,13 -0,21	$ \begin{vmatrix} -0,03 \\ -0,02 \\ -0,04 \end{vmatrix} $	$^{+2,09}_{+2,02}_{+2,62}$	+1,44 +1,40 +1,84	-0,12 -0,11 -0,17	-0,02 -0,02 -0,03	0,15 +0,83	+0,45 	+0,02	+0,02 - +0,002

TABLE 2. Values of ¹⁹F NMR Chemical Shifts and of Induction and Resonance Constants of 9-o-, 9-m-, and 2-p-Carboranyl Groups

p-HCB₁₀H₉(2-I)CH + m, p-FC₆H₄MgBr $\xrightarrow{\text{EtsO}} p$ -HCB₁₀H₉-2-(m, p-C₆H₄F)CH (V), (VI)

The properties of the obtained compounds are given in Table 1. On the basis of the ¹⁹F chemical shifts of compounds (I)-(VI) the σ_i and σ_R° for the 9-o-, 9-m-, and 2-p-carboranyl groups were calculated by the Taft method [9] (Table 2). As can be seen from Table 2, the 9-o- and 9-m-carboranyl groups in the studied solvents have a +I effect, in which connection the 9-o group is a stronger electron donor than the 9-m group, which is in agreement with the data given in [4-6].

The obtained results confirm the postulation [4] that the σ_i value of the 9-m-carboranyl group, determined by the Charton method, is high and does not reflect the real value of the electron-donor effect. In the case of the 2-p-carboranyl group the value of the effect is small, and it can be assumed that in its electronic effect this group should practically not differ from the H atom. When going from such solvents as CCl₄ and CHCl₃ to THF the value of the electron-donor effect of the 9-o- and 9-m-carboranyl groups increases somewhat, which is related to an increase in the electron density on the B atoms of the carborane nuclei due to the formation of a hydrogen bond involving the CH group of the carborane and the O atom of THF. A similar phenomenon was observed in the case of the 3-o- and 2-m-carboranyl groups.

EXPERIMENTAL

The GLC analysis was run on a Tswett-4 chromatograph equipped with a katharometer, and using a 4 mm \times 2 m column packed with 5% SE-30 deposited on Chromaton N-AW-HMDS, a temperature of 180-220°, and helium as the carrier gas. The ¹⁹F NMR spectra were measured on a Varian XL-100 spectrometer (94.1 MHz) at 23° using dilute solutions of the compounds (0.2 M) from C₆H₅F as the external standard in the same solvent and the same concentration.

General Method for Obtaining 9-(m- and p-Fluorophenyl)-o- and m-Carboranes (I)-(IV). A mixture of 2.7 g (10 mmoles) of 9-I-carborane, 33.3 ml of a 1.2 M solution (40 mmoles) fluorophenylmagnesium bromide, and 0.14 g (0.2 mmole) of $(Ph_3P)_2PdCl_2$ in 50 ml of abs. ether was refluxed for 30 h. After cooling to 20° the reaction mass was diluted with 25 ml of water, the organic layer was separated, washed in succession with dilute HCl solution and water, and the ether layer was separated and dried over Na₂SO₄. After distilling off the ether the residue was chromatographed on a 30 × 3 cm column packed with Chemapol silica gel (100/160 μ m), using a 7:3 petroleum ether-benzene mixture as the eluant. The yield of the products was 60-75%.

<u>General Method for Obtaining 2-(m- and p-Fluorophenyl)-p-carboranes (V), (VI).</u> A mixture of 1 g (3.7 mmoles) of 2-iodo-p-carborane, 14.8 mmoles of fluorophenylmagnesium bromide, and 0.1 g (0.14 mmoles) of $(Ph_3P)_2PdCl_2$ in 30 ml of abs. ether was refluxed for 60 h. Then the reaction mass was cooled, diluted with 20 ml of water, the organic layer was separated, washed in succession with dilute HCl solution and water, and the ether layer was separated and dried over Na₂SO₄. After distilling off the ether the residue was chromato-graphed on a 40 × 3 cm column packed with Chemapol silica gel (100/160 μ m), using hexane as the eluant. The yield of the products was 68-79%.

CONCLUSIONS

1. We effected the synthesis of the m- and p-(fluorophenyl)-9-o-, 9-m-, and 2-p-carboranes from the m- and p-FC₆H₄MgBr and 9-I-o-, 9-I-m-, and 2-I-p-carboranes in the presence of $(Ph_3P)_2PdCl_2$.

2. On the basis of the values of the ¹⁹F chemical shifts of the m- and p-fluorophenyl-9-o-, 9-m-, and 2-p-carboranes in CCl₄, CHCl₃, and THF we calculated the σ_i and σ_R° constants of the 9-o-, 9-m-, and 2-p-carboranyl groups by the Taft method.

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ADDITION OF ACETYLACETONE TO

ACYL(AROYL) ISOCYANATES

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Previously [1] it was shown that trichloroacetyl isocyanate (I) reacts with acetylacetone to give carbamate (II). On the examples of the subsequently studied reactions of acyl(aroyl) isocyanates with some β -dicarbonyl compounds it was established that the direction of adding isocyanates is determined not only by the ability of the β -dicarbonyl compounds to undergo keto-enol tautomerism, but also by their dual reactivity [2, 3]. This caused us to make a detailed study of the reaction of acyl(aroyl) isocyanates with acetylacetone as a simple model of a β -diketone.

As was mentioned above, (I) reacts with acetylacetone to give (II), in which connection the C-addition product was not isolated directly from the reaction mixture. The IR spectrum of (II) is given in [1]. An analysis of the PMR spectrum of (II) disclosed that (II) is a mixture of configuration isomers Z : E = 1 : 3, which follows from the ratio of the integral intensities of the signals of two types of methine protons at δ 6.18 and 6.62 ppm (CDCl₃).



It is known [4-6] that in the case of trisubstituted ethylenes the chemical shifts are informative for determining the configuration, and not the long-range spin-spin coupling constants, since the latter are determined by more than the geometry of the C=C bond. According to these data, the chemical shifts of the methyl protons of trisubstituted ethylenes are most frequently encountered further upfield for the E than for the Z isomers ($\Delta\nu \approx 0.20$ -0.30 ppm), while for the vinyl protons the reverse is true ($\Delta\nu \approx 0.50$ -0.90 ppm). In the case of (II) the $\Delta\nu$ value for the vinyl proton of the Z and E isomers corresponds to the literature data, whereas the $\Delta\nu$ value for the CH₃C=C protons is a total of only 0.05 ppm (δ , 2.53 and 2.58 ppm), which apparently can be explained by the deshielding effect of the acylamido group. The use of the IR spectral data to confirm

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