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4-o-CARBORANYLPYRYLIUM PERCHLORATES AND STABLE FREE RADICALS BASED ON THEM

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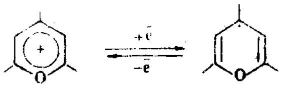
The corresponding o-carboranylpyrylium perchlorates were obtained from 4H-pyrans of the o-carborane series under the influence of 70% $HClO_4$ in acetic anhydride or 2,2',4,4'-tetramethoxydiphenylammonium perchlorate. The carboranylpyranyl free radicals were studied by EPR spectroscopy, and it was shown that the unpaired electron is localized in the carborane ring.

The EPR spectra of a number of pyranyl free radicals formed in the reduction of 2,4,6-trisubstituted pyrylium cations have been described [1-5]. The accessibility of these radicals promises to make them convenient one-electron reducing agents for organic synthesis, since their extremely facile conversion to pyrylium salts is generally a specific feature of their behavior [4]:



The chemical transformations of this unique class of free radicals have proved to be extremely interesting [4], and from an analysis of their EPR spectra one can conclude that the properties of pyranyl radicals should depend substantially on the nature of the substituents in the starting pyrylium salt. Thus the unpaired electron in the 2,4,6-triphenylpyranyl radical is delocalized over the entire molecule [3], while its tri-tert-butyl analog is a "rigid" C-fixed radical with a strongly shielded reaction center [5]. In this connection, we decided to obtain 4-o-carboranylpyranyl radicals, since the bulky icosahedral system of carborane should create additional possibilities for stabilization through its electron-acceptor properties.

The reduction of the previously described 4-o-carboranylpyrylium hexachloroantimonates [6] did not enable us to obtain sufficiently resolved EPR spectra (evidently because of splittings from the magnetic nuclei of the gegenion). We were unable to replace the anion by the action of 70% $HClO_4$ because of the low solubilities of the hexachloroantimonates.

The necessary pyrylium perchlorates with carborane substituents in the 4 position were obtained from o-carboranylpyrans (I) (Table 1), by the action of 2,2',4,4'-tetramethoxydiphenylammonium perchlorate on them. Pyrylium salts can also be obtained by the usual method,

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TABLE 1. 4-o-Carboranyl-4H-pyrans

Compound	R	R′	mp, °C (from CH_3NO_2)	IR spectrum, cm^{-1}	PMR spectrum, δ, ppm	Found, %			Empirical formula	Calc., %			Yield, %
						C	H	B		C	H	B	
Ia	H	$(CH_3)_3C$	119—121	2600, 1700	1,07 [(s, 18H, $(CH_3)_3C$]: 4.52 (d, 2H, 3,5-H): 3.50 (t, 2H, 4-H: CH$_{\text{carb}}$)	53,2	9,8	31,9	$C_{15}H_{32}B_{10}O$	53,5	9,6	32,1	25
Ib	H	C_6H_5	212—215	2600, 1690, 1500	7,20—7,80 (m, 10H, Ph); 5,45 (d, 2H, 3,5-H): 3,92 (t, 1H, 4-H): 3,67 (s, 1H, CH$_{\text{carb}}$)	60,2	6,2	28,4	$C_{19}H_{34}B_{10}O$	60,6	6,4	28,7	53
Ic	CH_3	$(CH_3)_3C$	121—123	2600, 1700	1,10 [(s, 18H, $(CH_3)_3C$)]; 4,62 (d. 2H, 3,5-H); 3,50 (t, 1H, 4-H); 1,92 (s, 3H, CH_3)	55,1	9,8	30,8	$C_{16}H_{34}B_{10}O$	54,8	9,8	30,8	80

TABLE 2. 4-o-Carboranylpyrylium Perchlorates

Compound	R	R′	mp, °C*	IR, spectrum, cm^{-1}	PMR spectrum, δ, ppm	B found, %	Empirical formula	B calc., %	Yield, % (method)
IIa	H	$(CH_3)_3C$	265 (expl)	2600, 1630, 1530, 1100	1,16 [s, 18H, $(CH_3)_3C$]; 4,20 (s, 1H, CH$_{\text{carb}}$); 7,57 (s, 2H, 3,5-H)	24,6	$C_{15}H_{31}B_{10}ClO_5$	24,8	58 (A)
IIb	H	C_6H_5	255 (expl.)	2600, 1630, 1540, 1500, 1490, 1480, 1100	†	22,7	$C_{19}H_{23}B_{10}ClO_5$	22,7	50 (A)
IIc	CH_3	$(CH_3)_3C$	265 (expl.)	2600, 1645, 1540, 1100	1,17 [s, 18H, $(CH_3)_3C$]; 1.44 (s, 3H, CH_3); 7,72 (s, 2H, 3,5-H)	24,2	$C_{16}H_{33}B_{10}ClO_5$	24,1	50 (A)
IId	C_6H_5	$(CH_3)_3C$	214—218	2600, 1630, 1535, 1100	0,87 [s, 18H, $(CH_3)_3C$]; 6,85—7,50 (m, 7H, Ph, 3,5-H	20,9	$C_{21}H_{35}B_{10}ClO_5$	21,2	60 (A)
IIe	C_6H_5	C_6H_5	257 (expl.)	2600, 1630, 1520, 1100	6,80—7,85 (m, Ph, 3,5-H)	20,0	$C_{25}H_{27}B_{10}ClO_5$	19.6	55 (A) 20 (B)
IIf	C_6H_5	p-$CH_3OC_6H_4$	270 (expl.)	2600, 1610, 1520, 1100	3,62 (s, 6H, CH_3O): 6,70—7,90 (m, 15H, Ph, p-$CH_3OC_6H_4$, 3,5-H)	18,0	$C_{27}H_{31}B_{10}ClO_7$	17,7	34,5 (A) 37,5 (B)

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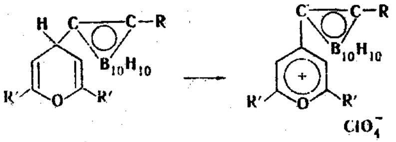
*The compounds were crystallized: IIa,c,d,f from glacial acetic acic, IIb from a mixture of glacial acetic acid with acetic anhydride, and IIe from acetic anhydride.

†The PMR spectrum could not be recorded because of the low solubility of this compound.

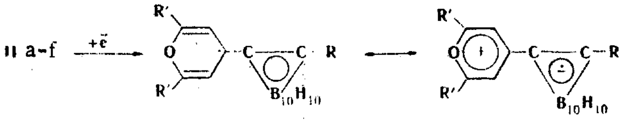
viz., by the action of 70% perchloric acid in the acetic anhydride on carboranylpyrans. However, in this case one must thoroughly purify the starting pyran, since otherwise the carborane fragment is split out, and the pyran ring opens to give a saturated carboranyl 1,5-diketone.

We obtained a number of pyrylium perchlorates of the o-carborane series by these methods (Table 2).



I a-f II a-f

Free radicals that have virtually identical EPR spectra are formed in the reduction of 4-o-carboranylpyrylium perchlorates with zinc in acetonitrile or tetrahydrofuran (THF) (at 20°C):



The observed EPR spectra can be interpreted as being the result of interaction of the unpaired electron with six boron atoms (^{11}B, S = 3/2) regardless of the nature of R and R', i.e., the unpaired electron is localized completely on the o-carborane ring. The theoretical spectrum in the case of equivalence of the six boron atoms should consist of 19 lines with an intensity ratio of 1:6:21:56:120:216:336:456:546:580:546:456:336:216:120:56:21:6:1; however, only 15 lines are actually observed because of the significant difference in the intensities (1:580) of the extreme and middle components. Consequently, of the resonance structures presented above, the right-hand zwitterion radical predominates markedly. Under anaerobic conditions the lifetime of the radicals obtained is virtually unlimited.

It is noteworthy that the EPR spectra of carboranylpyranyl radicals are similar on the whole to the spectra of the corresponding sterically hindered phenoxy radicals [7] but differ from them only with respect to the large constant of hyperfine coupling with the ^{11}B nucleus (a = 1.2 Oe).

EXPERIMENTAL

The IR spectra of thin layers of mineral oil suspensions of the synthesized compounds were recorded with a UR-20 spectrometer. The PMR spectra of carboranylpyrans I (in CCl_4 solutions) and carboranylpyrylium salts II (CF_3COOH solutions) were recorded at room temperature with a Tesla BS-467 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The protons of the B—H bonds are not resolved at operational frequencies of 60 and 80 MHz. The EPR spectra were recorded with an ER-09 radiospectrometer.

4H-o-Carboranylpyrans Id-f were obtained by the method in [6]. The boron content in the dangerously explosive o-carboranylpyrylium perchlorates was determined by spectrophotometry.

2,6-Di-tert-butyl-4-o-carboranyl-4H-pyran (Ia). 1-Lithio-o-carborane was obtained from 0.72 g (0.005 mole) of o-carborane and 0.005 mole of n-butyllithium (in benzene) in an argon atmosphere. Absolute ether was added to dissolve the precipitate, and 1.5 g (0.005 mole) of 2,6-di-tertbutylpyrylium perchlorate was added in small portions with stirring to the resulting solution, during which the pyrylium salt dissolved. The reaction mixture was treated with a cold solution of ammonium chloride, and the organic layer was washed with water and dried with $MgSO_4$. The solvents were removed, and the residue was triturated with alcohol and acetonitrile. The resulting precipitate was removed by filtration and recrystallized from nitromethane.

2,6-Diphenyl-4-o-carboranyl-4H-pyran (Ib). This reaction was similarly carried out with 0.72 g (0.005 mole) of o-carborane, 0.005 mole of n-butyllithium (in benzene), and 1.66 g (0.005 mole) of 2,6-diphenylpyrylium perchlorate. The pyrylium salt dissolved, after which the solvents were removed, and the residue was triturated with acetonitrile. The precipitate was removed by filtration and recrystallized from nitromethane.

2,6-Di-tert-butyl-4-o-methylcarboranyl-4H-pyran (Ic). This reaction was similarly carried out with 0.79 g (0.005 mole) of o-methylcarborane, 0.005 mole of n-butyllithium (in benzene), and 1.5 g (0.005 mole) of 2,6-di-tert-butylpyrylium perchlorate. The pyrylium salt dissolved, and the reaction mixture darkened. The solvents were removed, and the residue was triturated with alcohol. The precipitate was removed by filtration and recrystallized from nitromethane.

Method A. 2,6-Di-tert-butyl-4-o-carboranylpyrylium Perchlorate (IIa). A 0.1-ml (0.001 mole) sample of 70% $HClO_4$ was added to a suspension of 0.34 g (0.001 mole) of carboranylpyran Ia in 5 ml of acetic anhydride, and the mixture was refluxed until the solid dissolved. It was then cooled and diluted with a large volume of ether, and the precipitate was removed by filtration and recrystallized from glacial acetic acid.

Salts IIb-f were similarly obtained.

Method B. 2,6-Diphenyl-4-o-phenylcarboranylpyrylium Perchlorate (IIe). A mixture of 0.45 g (0.001 mole) of 2,6-diphenyl-4-o-phenylcarboranyl-4H-pyran and 0.39 g (0.001 mole) of immonium oxide perchlorate [8] in acetone was heated on a warm-water bath until the initially dark-green mixture turned brown, after which it was diluted with a large volume of ether and filtered. The filtrate was allowed to stand, and the resulting precipitate was removed by filtration.

2,6-Dianisyl-4-o-phenylcarboranylpyrylium Perchlorate (IIf). A 0.39-g (0.001 mole) sample of immonium oxide perchlorate was added to a solution of 0.51 g (0.001 mole) of 2,6-dianisyl-4-o-phenylcarboranyl-4H-pyran in acetone, during which the reaction mixture darkened. The mixture was diluted with ether, and the resulting precipitate was removed by filtration.

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