

CARBORANYLPYRANS AND CARBORANYLPYRYLIUM SALTS

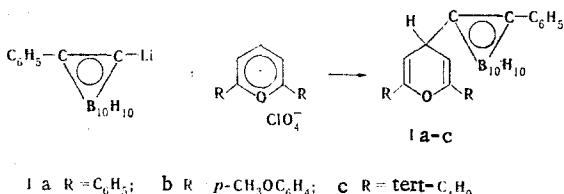
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Relatively difficult-to-oxidize 4-carboranylpyrans were obtained by the action of (phenyl-*o*-carboranyl)lithium on 2,6-disubstituted pyrylium salts. The conversion of the 4-carboranylpyrans to the corresponding 4-carboranylpyrylium salts is achieved by the action of a one-electron oxidizing agent — tris(*p*-bromophenyl)aminium hexachloroantimonate. The 4-(*o*-carboranyl)pyrylium salts readily undergo one-electron electrochemical reduction. It is assumed that the first step in dehydrogenation of the pyrans is one-electron transfer.

It should have been expected that 4H-pyrans that contain strong electron-acceptor groupings in the 4 position have specific properties that differ from the properties of their analogs, since the "hydride" lability of the general hydrogen atom will be reduced in this case. To verify this assumption we undertook the synthesis of some 4-(*o*-carboranyl)pyrans and studied their conversion to the corresponding pyrylium salts. It is known that stable icosahedral *o*-carboranes are characterized by a pronounced electron deficit [1].

For the synthesis of the pyrans we used a method that is, in principle, similar to the method known in the chemistry of pyrylium salts [2] — alkylation of unsubstituted pyrylium cations.



4-(C-Phenyl-*o*-carboranyl)pyrans Ia-c were obtained in 60-86% yields in the case of a stoichiometric reagent ratio (in benzene). In contrast to many known 4H-pyrans, the compounds obtained in this research are sufficiently stable with respect to oxidation and are readily purified. Their structures were confirmed by the IR spectra and PMR data (Table 1).

The stability of the carboranylpyrans with respect to oxidation is graphically displayed in their polarographic behavior.* For example, whereas 2,6-diphenylpyran is oxidized on a stationary platinum microelectrode in a sodium tetrafluoroborate base electrolyte at 1.5 V, under the same conditions 4-phenylcarboranyl-2,6-diphenylpyran is oxidized only at 2.0 V. Replacement of the phenyl groups in the 2 and 6 positions by tert-butyl groups facilitates oxidation somewhat ($E_p = +1.6$ V). Carboranylpyran Ib is oxidized at 1.8 V under the same conditions.

We were unable to accomplish the transition from the carboranylpyrans to carboranylpyrylium salts by the action of trityl or acetyl perchlorate, which are usually employed for this purpose, although reactions of this type are traditionally classified as "hydride ion" detachment.

However, it is characteristic that the 4-carboranylpyrans obtained are relatively easily converted to the corresponding 4-carboranylpyrylium cations under the influence of a typical one-electron oxidizing agent — the tris(*p*-bromophenyl)aminium cation radical. Better results were obtained with the readily accessible tris(*p*-bromophenyl)aminium hexachloroantimonate. It is evident that these transformations are initiated by one-electron transfer from pyran to the oxidizing agent and cannot be associated with the actual transfer of a hy-

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TABLE 1. 4-(Phenyl-o-carboranyl)-2,6-diaryl(alkyl)pyrans

Com- ound	R	mp, °C ^a	Found, %			Empirical formula	Calculated, %			IR spec- trum, ν , cm ⁻¹	PMR spectrum, ^b δ, ppm	Yield, %
			C	H	B		C	H	B			
Ia	C ₆ H ₅	132—134.5	66.7	6.5	23.8	C ₂₅ H ₂₈ B ₁₀ O	66.3	6.2	23.9	2600 1695 1610 1585 1500	C ₆ H ₅ : 7.00—7.85 (m) β-H: 5.15 (d) γ-H: 3.27 (t)	75
Ib	p-CH ₃ OC ₆ H ₄	159—161	63.4	6.8	20.6	C ₂₇ H ₃₂ B ₁₀ O ₃	63.3	6.3	21.1	2600 1695 1615 1585 1525	C ₆ H ₅ : 7.10—7.77 (m) β-H: 4.97 (d) γ-H: 3.30 (t) CH ₃ : 3.75 (s) C ₆ H ₄ : 6.80 (d) 7.40 (d) ^c	60
Ic	tert-C ₄ H ₉	133—135	61.0	9.0	25.7	C ₂₁ H ₃₆ B ₁₀ O	61.1	8.8	26.2	2600 1700	C ₆ H ₅ : 7.17—7.82 (m) β-H: 4.29 (d) γ-H: 2.77 (t) (CH ₃) ₃ C: 1.00 (s)	98

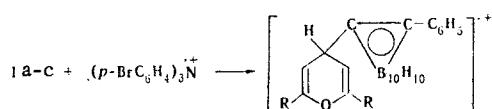
^aFrom nitromethane.^bThe signals of the protons bonded to boron are not resolved at operating frequencies of 60 and 80 MHz.^cThis signal is overlapped with the multiplet.

TABLE 2. 4-(Phenyl-o-carboranyl)-2,6-diaryl(alkyl)pyrylium Hexachloroantimonates

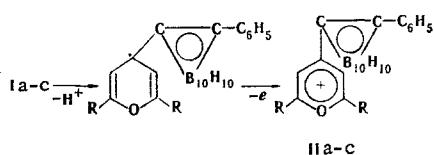
Com- ound	R	mp, °C ^a (dec.)	Found, %		Empirical formula	Calc., %		IR spect., ν , cm ⁻¹	Yield, %
			C	H		C	H		
IIa	C ₆ H ₅	195—207	38.3	3.8	C ₂₅ H ₂₇ B ₁₀ Cl ₆ OSb	38.2	3.5	2600 1630 1600 1585 1510	78
IIb	p-CH ₃ OC ₆ H ₄	216—222	38.6	4.8	C ₂₇ H ₃₁ B ₁₀ Cl ₆ O ₃ Sb	38.3	3.6	2600 1630 1610 1580	76
IIc	tert-C ₄ H ₉	212—215	33.6	5.6	C ₂₁ H ₃₅ B ₁₀ Cl ₆ OSb	33.8	4.7	2600 1630 1530	47

^aFrom glacial acetic acid—acetic anhydride (1:1).

dride ion. The aminium cation radical is not, in principle, capable of accepting either a hydride ion or a hydrogen atom; the only possible first step in the dehydrogenation initiated by it is one-electron transfer:

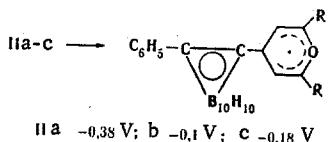


In the absence of an acceptor of the atomic hydrogen that is formed in this step the cation radical cannot be converted to a pyrylium cation through detachment of a hydrogen atom; the alternative is to assume the hydrogen is split out in the form of a proton with subsequent oxidation of the pyran radical:



The carboranylpyrylium hexachloroantimonates (IIa-c, Table 2) obtained in this way are practically insoluble in trifluoroacetic acid and its anhydride, and this made it impossible to study their PMR spectra.

Whereas the electrochemical oxidation of the 4-carboranylpyrans proceeds with relative difficulty, the reduction of the corresponding 4-carboranylpyrylium cations on a dropping mercury electrode in acetonitrile in a sodium perchlorate base electrolyte proceeds at record-breaking low potentials:



For comparison it can be pointed out that 2,6-di-*tert*-butylpyrylium and 2,4,6-triphenylpyrylium perchlorates are reduced under the same conditions at, respectively, -0.74 and -1.49 V. It is characteristic that phenylcarborane is reduced at -1.7 V [in a $(CH_3)_4N^+ClO_4^-$ base electrolyte] under these conditions.

Since methods for the conversion of pyrylium salts to various heterocyclic compounds have been well worked out at present [2], this opens up the possibility of the preparation of new types of carborane derivatives of heterocycles.

EXPERIMENTAL

The IR spectra of $CHCl_3$ solutions of the carboranylpyrans and thin layers of mineral oil suspensions of the carboranylpyrylium salts were recorded with a UR-20 spectrometer. The PMR spectra of Ia,c were recorded at room temperature with a Tesla BS-467 spectrometer (60 MHz), and the spectrum of carboranylpyran Ib was recorded at 60° with a Tesla BS-487c spectrometer (80 MHz); the solvent was CCl_4 , and the internal standard was hexamethyldisiloxane. The electrochemical oxidation was carried out with a PPT-1 polarograph; reduction was accomplished with an OP-2 oscilloscopolarograph.

4-(Phenylcarboranyl)-2,6-diphenyl-4H-pyran (Ia). A solution of (phenyl-*o*-carboranyl)lithium [3] [from 2.2 g (0.01 mole) of phenyl-*o*-carborane and butyllithium] in benzene was added with stirring in an argon atmosphere to a suspension of 3.3 g (0.01 mole) of 2,6-diphenylpyrylium perchlorate in benzene, after which the mixture was stirred at room temperature for 20 min, and the precipitated lithium perchlorate was removed by filtration. The solvent was removed from the filtrate, and the residue was triturated in alcohol. Solid pyran Ia was removed by filtration and recrystallized from nitromethane to give 3.4 g (75%) of Ia.

Compounds Ib and Ic were similarly obtained.

4-(Phenylcarboranyl)-2,6-diphenylpyrylium Hexachloroantimonate (IIa). A mixture of 0.45 g (0.001 mole) of carboranylpyran and 0.82 g (0.001 mole) of tris(*p*-bromophenyl)aminium hexachloroantimonate [4] in absolute dioxane was refluxed in an argon atmosphere until the intensely blue color of the cation radical vanished. The mixture was then cooled, and the precipitated pyrylium salt IIa was removed by filtration and recrystallized from glacial acetic acid-acetic anhydride (1:1) to give 0.61 g (78%) of IIa.

Salts IIb and IIc were similarly obtained.

LITERATURE CITED

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