MONO- AND BISPYRYLIUM SALTS OF THE o- AND m-CARBORANE SERIES

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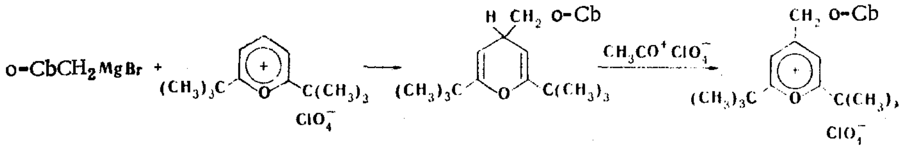
It was established that 4H-pyrans of the carborane series, which are readily obtained by organometallic synthesis with the aid of Grignard reagents, as well as lithium derivatives of 12-carboranes, are successful starting compounds for the systhesis of carboranylpyrylium salts. 2,6-Di-tert-butyl-4-o-carboranylmethylpyrylium perchlorate and o- and m-carboranylbispyrylium bishexachloroantimonates were obtained from the corresponding 4H-pyrans.

The aim of our research was to develop methods for the synthesis of pyrylium salts that contain a bulky electron-deficient carboranyl grouping.* The methods for the preparation of pyrylium salts can presently be classified under one of the following three general methods: synthesis from compounds that contain a pyran ring, reactions involving acylation of unsaturated compounds and ketones, and reactions involving condensation of carbonyl compounds [1]. In the course of the research it was ascertained that the most successful starting compounds for the synthesis of carboranylpyrylium salts are carboranyl-4H-pyrans. We have previously obtained 4-o-carboranylpyrylium hexachloroantimonates [2] and perchlorates [3] from o-carboranylpyrans. The use of accessible lithium derivatives of o-carborane in the synthesis of the starting pyrans makes this method particularly convenient.

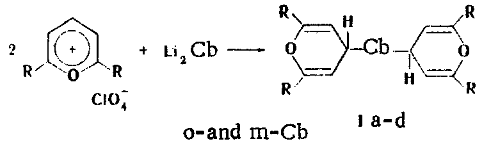
To expand the possibilities for the use of this method we synthesized 4H-pyran with an o-carboranylmethyl substituent starting from a Grignard reagent [4], obtained from 1-bromomethyl-o-carborane, and 2,6-di-tert-butylpyrylium perchlorate.

The thoroughly purified pyran was converted to the corresponding pyrylium salt by the action of acetic anhydride and 70% perchloric acid:



Splitting out of a carborane fragment occurs in the case of direct treatment with acetyl perchlorate of the reaction mixture obtained via the Grignard reaction, as a result of which the starting γ-unsubstituted pyrylium salt and a saturated carboranyl δ-diketone are isolated.

We also obtained o- and m-carboranylbis-4H-pyrans Ia-d via the following scheme (Table 1):



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*The formula  , used to designate o-carborane, will subsequently be written o-Cb, while the formula $HCB_{10}H_{10}CH$ used to designate m-carborane ($1,7-C_2B_{10}H_{12}$) will subsequently be written m-Cb.

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TABLE 1. Bis-4H-pyrans of the o- and m-Carborane Series

Compound	Cb	R	mp, °C*	IR spectrum, cm^{-1}	PMR, δ, ppm	Found, %			Empirical formula	Calc., %			Yield, %
						C	H	B		C	H	B	
Ia	o-	$(CH_3)_3C$	185—188	2600 (B—H); 1700 (C=C)	1,05 [s, 36H, $(CH_3)_3C$]; 3,50 (t, 2H, 4-H); 4,54 (d, 4H, 3-H, 5-H)	63,2	9,3	19,9	$C_{28}H_{52}B_{10}O_2$	63,6	9,9	20,4	81
Ib	o-	C_6H_5	214—218	2600; 1690	7,18—7,82 (m, 20H, Ph); 4,10 (t, 2H, 4-H); 5,50 (d, 4H, 3-H, 5-H)	71,4	5,6	17,9	$C_{36}H_{36}B_{10}O_2$	71,0	6,0	17,6	60
Ic	m-	$(CH_3)_3C$	127—130	2600; 1700	1,07 [s, 36H, $(CH_3)_3C$]; 3,14 (t, 2H, 4-H); 4,48 (d, 4H, 3-H, 5-H)	63,8	10,3	20,4	$C_{28}H_{52}B_{10}O_2$	63,6	9,9	20,4	80
Id	m-	C_6H_5	168—170	2600; 1700	—	69,7	6,3	17,2	$C_{36}H_{36}B_{10}O_2$	71,0	6,0	17,6	57

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*The compounds were crystallized: Ia from benzene—alcohol, Ib from nitromethane, Ic from benzene—alcohol or acetone, and Id from benzene—alcohol or benzene—chloroform.

TABLE 2. o- and m-Carboranylbispyrylium Bishexachloroantimonates

Compound	Cb	R	mp, (dec.), °C*	IR spectrum, cm^{-1}	Found, %		Empirical formula	Calc., %		Yield, %
					C	H		C	H	
II a	o-	$(CH_3)_3C$	168—175	2600; 1625; 1530	26,7	4,4	$C_{28}H_{50}B_{10}Cl_{12}O_2Sb_2$	27,1	4,2	67
II b	o-	C_6H_5	>175	2600; 1610; 1530; 1490	33,5	3,2	$C_{36}H_{34}B_{10}Cl_{12}O_2Sb_2$	33,6	2,6	55
II c	m-	$(CH_3)_3C$	>180	2600; 1625; 1525	26,5	4,2	$C_{28}H_{50}B_{10}Cl_{12}O_2Sb_2$	27,1	4,2	98

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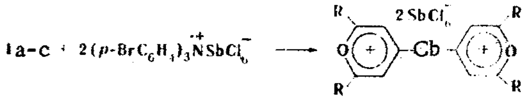
*Compounds IIa, b were purified by reprecipitation from acetone by the addition of ether, while IIc was purified by reprecipitation from nitromethane.

The bispyrans are readily converted to o- and m-carboranylbispyrylium bishexachlorantimonates (Table 2) under the influence of a one-electron oxidizing agent, viz., tris(p-bromophenyl)aminylium hexachlorantimonate:



o- and m-Cb

II a-c

The bishexachlorantimonates cannot be converted to bisperchlorates by the action of 70% $HClO_4$ (in acetone, acetic acid, or acetonitrile) because of the low solubility of the bishexachlorantimonates; their PMR spectra were not recorded, for the same reason.

It is characteristic that the carboranylbispyrylium bishexachloroantimonates undergo cleavage of the C—C bond of the carborane and pyrylium fragments when they are refluxed with excess 70% $HClO_4$ (in glacial acetic acid), as a result of which γ-unsubstituted pyrylium perchlorates are isolated. Cleavage of the C—C bond between the o-carborane ring and the functional group of carborane derivatives under the influence of nucleophilic agents is a well-known fact [5-7] In our case cleavage of the C—C bond in carborane derivatives occurs in strongly acidic media. This observation confirms our assumption that the C—C bond between the strongly electron-acceptor carboranyl grouping and the positively charged carboxonium cation is capable of protolysis; under certain conditions this makes the formation of a pyrylium cation without a carborane fragment preferable.

Carboranylpyrylium bisperchlorates are obtained in low yields by the action of acetic anhydride and 70% $HClO_4$ on the bispyrans. Treatment of the carboranylbis-4H-pyrans with trityl perchlorate (in acetonitrile) does not lead to the production of pyrylium salts.

EXPERIMENTAL

The IR spectra of thin layers of mineral oil suspensions (solutions in $CHCl_3$ in the case of bispyrans Ia-c) were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the carboranylbis-4H-pyrans in CCl_4 were recorded with a Tesla BS-467 spectrometer (60 MHz) at room temperature with hexamethyldisiloxane as the internal standard.

1,2-Bis(2,6-di-tert-butyl-4H-pyranyl)-o-carborane (Ia). 1,2-Dilithio-o-carborane was obtained from 0.72 g (0.005 mole) of o-carborane in absolute benzene and n-butyllithium (in benzene), after which absolute ether was added until the precipitate dissolved. A 3-g (0.005 mole) sample of 2,6-di-tert-butylpyrylium perchlorate was then added in small portions in a stream of argon to the resulting solution, during which the pyrylium salt dissolved. The solvents were removed from the reaction mixture, and the residue was triturated with alcohol. The resulting precipitate was removed by filtration and recrystallized from alcohol—benzene. The yield was 2.15 g (81%).

Bispyrans Ib-d were similarly obtained.

o-Carboranyl-1,2-bis(2,6-di-tert-butyl)pyrylium Bishexachloroantimonate (IIa). A mixture of 0.53 g (0.001 mole) of bispyranyl-o-carborane Ia and 1.64 g (0.002 mole) of tris(p-bromophenyl)aminylium hexachlorantimonate [8] in dioxane was refluxed until the intense blue color of the cation radical disappeared. The mixture was then cooled and diluted with a large volume of ether, and the resulting precipitate was removed by filtration and reprecipitated from acetone by the addition of ether. The product was obtained in 67% yield.

Salts IIb, c were similarly obtained.

Cleavage of the C—C Bond in o-Carboranyl-1,2-bis(2,6-diphenylpyrylium) Bishexachlorantimonate. A 0.7-ml sample of 70% perchloric acid was added to a suspension of 0.4 g of bishexachloroantimonate IIb in glacial acetic acid, and the mixture was refluxed until the bispyrylium salt dissolved, during which the mixture turned dark-green. The precipitate that formed after cooling and dilution with ether was identified as 2,6-diphenylpyrylium perchlorate. The yield was 0.1 g.

2,6-Di-tert-butyl-4-o-carboranylmethyl-4H-pyran. A 3-g (0.001 mole) sample of 2,6-di-tert-butylpyrylium perchlorate was added in small portions in a stream of argon to a Grignard reagent (in ether), obtained from 2.36 g (0.01 mole) of 1-bromomethyl-o-carborane and 0.26 g (0.011 mole) of magnesium, during which the pyrylium salt dissolved. The mixture was treated with a saturated aqueous solution of ammonium chloride, washed with water, and dried with $MgSO_4$. The solvent was removed, the residue was triturated with alcohol, and the resulting precipitate was removed by filtration to give 1.2 g (35%) of a product with mp 119-121°C (from nitromethane). IR spectrum: 2600 (B—H) and 1705 cm^{-1} (C=C). PMR spectrum: 1.02 [s, 18H, $(CH_3)_3C$], 4.45 (d, 2H, 3-H and 5-H), 2.97 (s, 1H, 4-H), 3.53 (s, 1H, CH_{carb}), and 2.15 (s, 2H, CH_2). Found, %: C 54.5; H 9.8; B 31.0. $C_{16}H_{34}B_{10}O$. Calculated, %: C 54.8; H 9.8; B 30.8.

2,6-Di-tert-butyl-4-o-carboranylmethylpyrylium Perchlorate. A 0.1-ml (0.001 mole) sample of 70% $HClO_4$ was added to 0.35 g (0.001 mole) of 2,6-di-tert-butyl-4-o-carboranylmethyl-4H-pyran in 5 ml of acetic anhydride, and the reaction mixture was heated to the boiling point. It was then cooled and diluted with a large volume of ether, and the resulting precipitate was removed by filtration to give 0.11 g (25%) of a product with mp 255°C (from glacial acetic acid). IR spectrum: 2600 (B—H); 1630 and 1540 (pyrylium cation); 1100 cm^{-1} (ClO_4^-). Found, % B 24.3. $C_{16}H_{33}B_{10}ClO_5$. Calculated, %: B 24.1.

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PYRYLOCYANINES. 9.* ISOBENZOPYRYLOCYANINES

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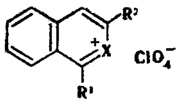
Polymethine dyes with symmetrical and unsymmetrical structures, viz., 3-phenyl-2-benzopyrylium derivatives, were synthesized. Their colors are discussed.

Polymethine dyes that contain a 2-benzopyrylium ring were unknown up until now. Within our plan to investigate the dependence of the color on the chemical structure in the pyrylocyanine series, it seemed of interest to synthesize isomeric flavylocyanine [2, 3] dyes that contain 3- and 1-phenyl-substituted 2-benzopyrylium residues. In the synthesis of dyes of the first type we started from 1-methyl-3-phenyl-2-benzopyrylium perchlorate (Ia) or 1-formylmethylene-3-phenyl-2-benzopyran (III). Oxonium salt Ia was obtained by the action of methylmagnesium iodide on 3-phenylisocoumarin.



I a-c

I a X=O, R^1=CH_3, R^2=C_6H_5; b X=O, R^1=C_6H_5, R^2=CH_3; c X=NCH_3, R^1=C_6H_5, R^2=CH_3

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*See [1] for communication 8.

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