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REACTIONS OF 4-(o-CARBORANYL)PYRYLIUM SALTS WITH NUCLEOPHILIC AGENTS. SYNTHESIS OF NITROGEN HETEROCYCLES WITH AN o-CARBORANYL SUBSTITUENT

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Nitrogen heterocycles, viz., pyridines, pyridinium salts, diazepine, and pyrazoles, with an o-carboranyl substituent were obtained by reaction of 4-(o-carboranyl)-pyrylium perchlorates with nitrogen-containig nucleophilic agents, viz., ammonia, primary amines, hydrazine, and phenylhydrazine. Opening of the pyrylium ring without involvement of the carborane ring occurs under the influence of bases.

Despite the fact that the synthetic chemistry of 12-carboranes has undergone active development in recent years, few carboranyl-substituted heterocycles are known [1-6]. The described heterocycles generally contain a carboranylmethyl grouping; the presence of a separating CH_2 group substantially reduces the effect of the carborane ring on the heterocyclic fragment as a consequence of the pronounced decrease in the inductive effect [7].

It seemed of interest to us to introduce a carboranyl grouping directly bonded to the heterocyclic ring as a substituent in nitrogen heterocycles. For this, we used carboranylpyrylium salts, which, like other pyrylium salts [8], should form various heterocyclic derivatives under the influence of N-containing nucleophilic agents.

The starting 4-(o-carbornayl)pyrylium perchlorates contained phenyl or tert-butyl groups in the 2 and 6 positions. Little study has generally been devoted to the transformations of pyrylium salts that contain bulky tert-butyl groups in the α,α'-positions of the pyrylium ring [9-11]. It is assumed that the outcome of the reaction is determined by the size of the α substituents rather than by their electronic effect [11].

Under the influence of ammonia, 2,6-diphenyl-4-(phenyl-o-carboranyl)pyrylium (Ia) and 2,6-di-tert-butyl-4-(methyl-o-carboranyl)pyrylium (Ib) salts are converted readily and in high yields to the corresponding pyridines, which can be used as characteristic derivatives for the identification of carboranylpyrylium perchlorates, since the latter explode when they are heated.

The action of primary amines of the aliphatic and aromatic series, viz., methylamine and aniline, leads to the production of the corresponding N-methyl- and N-phenylpyridinium perchlorates only when there are phenyl groups in the α,α' positions of the pyrylium ring. The presence of bulky tert-butyl groups in these positions hinders the indicated transformations. The reaction is realized in ethanol in the case of methylamine, while the use of glacial acetic acid as the solvent gave good results in the case of aniline.

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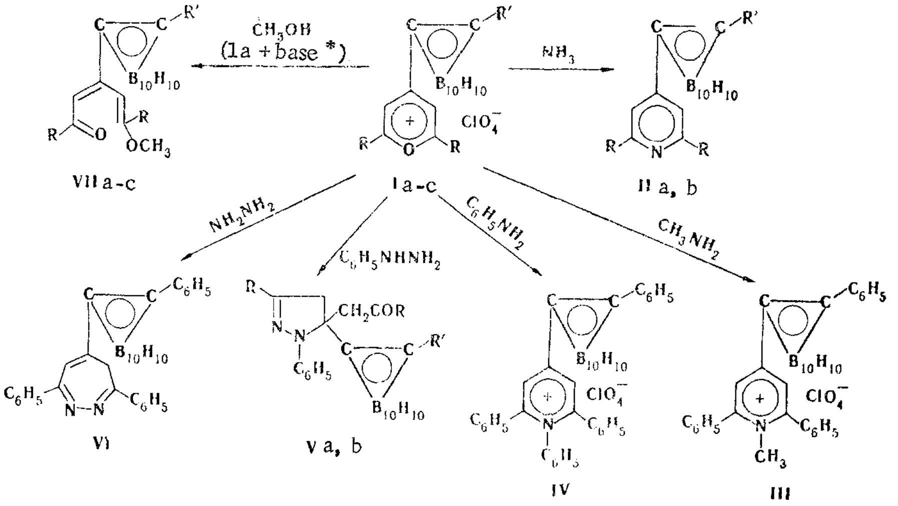
The conversion of pyrylium salt Ia to the previously undescribed nonsaltlike nitrogen-containing heterocyclic derivatives by the action of hydrazine and phenylhydrazine was carried out in methanol. The reaction of phenylhydrazine with salt Ia was also realized in glacial acetic acid, while the reaction with salt Ib was realized in benzene. Salt Ia gives a carboranyl-substituted diazepine on reaction with hydrazine. The products of the reaction of salts Ia and Ib with phenylhydrazine are carboranyl-substituted pyrazolines.

All of the IR spectra of the compounds obtained contain a band of stretching vibrations of B—H bonds of the carborane ring at 2600 cm^{-1}. The IR spectra of pyridines IIa, b contain bands at 1500-1600 cm^{-1}, which are characteristic for the vibrations of the pyridine ring, while a broad band at 1100 cm^{-1} (ClO_4^-) and bands at 1610-1630 and 1540-1580 cm^{-1}, which are due to the vibrations of pyridinium cations, are present in the IR spectra of pyridinium perchlorates III and IV. A singlet of protons of a methyl group (3.40 ppm) and a multiplet of aromatic protons (6.70-7.25 ppm) are observed in the PMR spectrum of III. The IR spectrum of diazepine VI is characteristized by the presence of very weak absorption bands of aromatic groupings at 1620 and 1500 cm^{-1}. The structures of carboranyl-substituted pyrazolines Va, b are confirmed by the presence in the IR spectra of the absorption band of a carbonyl group of a phenacyl fragment at 1680 cm^{-1} and absorption bands of a carbonyl group of a pivaloylmethyl fragment at 1700 cm^{-1}.



I, II, V, VII a R=R′=Ph; b R=CH_3, R′=t-C_4H_9; I, VII c R=Ph, R′=t-C_4H_9

*Base: $NaHCO_3$, CH_3ONa, $(C_2H_5)_3N$, $CH_3C\begin{smallmatrix}\diagup NH\\ \diagdown NH_2\end{smallmatrix}$, $C_6H_5C\begin{smallmatrix}\diagup NH\\ \diagdown NH_2\end{smallmatrix}$

The described reactions of carboranylpyrylium salts with N-containing compounds are realized readily at room temperature, and only the reaction of salt Ia with the weakly basic aniline requires heating. The reaction of this salt with phenylhydrazine (in methanol) also takes place with heating; the carborane ring, which usually undergoes destruction under the influence of trialkylamines, hydrazine, ammonia, piperidine, and alcoholic alkali [12], is not involved in this case. In order to reliably convince ourselves that the closo structure of carborane is retained in the process of the transformations of the pyrylium salts, we subjected perchlorate Ia to reaction with the following bases: sodium bicarbonate, sodium methoxide, and triethylamine (in methanol). Under the conditions of these reactions salt Ia undergoes ring opening to give the methyl ether of the enol form of the corresponding pentenedione. As in the case of other pyrylium salts, ring opening evidently occurs under the influence of atmospheric oxygen on the initially formed pyranyl free radical [13]; consequently, the nucleophilic agents used are one-electron reducing agents with respect to salts Ia and Ib.

The same diketone was obtained instead of the expected pyrimidines in the reaction of carboranylpyrylium salt Ia with acetamidine and benzamidine (in methanol).

4-(o-Carboranyl)pyrylium perchlorates that contain tert-butyl groups in the 2 and 6 positions react with methanol to give methyl ethers of the enol forms of pentenediones, in connection with which this solvent proved to be unsuitable as a medium for carrying out the reactions of these salts.

TABLE 1. Methyl Ethers of the Enol Forms of Carboranyl-Substituted Pentenediones

Compound	mp, °C	IR spectrum, cm^{-1}	PMR spectrum, δ, ppm	Found, %			Empirical formula	Calc., %			Yield, % (method)
				C	H	B		C	H	B	
VIIa	167–169	2600, 1640, 1560, 1490	6,75—7,75 (m, 15H, C_6H_5); 2,85 (s, 3H, CH_3O); 5,30 (s, 1H, =CH); 5,90 (s, 1H, =CH)	64,8	6,5	22,3	$C_{26}H_{30}B_{10}O_2$	64,7	6,3	22,4	Quantitative (A, C) 85 (D) 84 (E)
VIIb	80—82	2600, 1650, 1590	0,82 [s, 9H, $(CH_3)_3C$]; 1,09 [s, 9H, $(CH_3)_3C$]; 3,19 (s, 3H, CH_3); 1,77 (s, 3H, CH_3O); 5,12 (s, 1H, =CH); 5,47 (s, 1H, =CH)	53,4	9,0	28,6	$C_{17}H_{36}B_{10}O_2$	53,6	9,3	28,4	Quantitative
VIIc	94—96	2600, 1650, 1590	0,57 [s, 9H, $(CH_3)_3C$]; 0,95 [s, 9H, $(CH_3)_3C$]; 7,00—7,62 (m, 5H, C_6H_5); 2,50 (s, 3H, CH_3O); 4,92 (s, 1H, =CH); 5,25 (s, 1H, =CH)	59,4	8,5	24,7	$C_{22}H_{38}B_{10}O_2$	59,7	8,6	24,4	Quantitative

The structures of the methyl ethers of the enol forms of carboranyl-substituted pentenediones were confirmed by IR and PMR spectroscopy (see Table 1). In the PMR spectra the protons attached to the double bonds show up in the form of sharp singlets, in contrast to the methyl ether that was obtained from the 2,4,6-triphenylpyrylium salt [14], in the spectrum of which the indicated protons give two doublets (δ 6.50 and 5.74 ppm).

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the synthesized compounds were recorded with a Specord-71IR spectrometer. The PMR spectrum of a solution of III in CF_3COOH was recorded with a Tesla BS-487 spectrometer (60 MHz) at 20°C with hexamethyldisiloxane as the internal standard.

The starting carboranylpyrylium perchlorates (Ia-c) were obtained by the method in [15]. The individuality of the nonsaltlike products of conversion of the carboranylpyrylium salts was monitored by thin-layer chromatography (TLC) on Al_2O_3 (elution with benzene or benzene—hexane and development with concentrated H_2SO_4 or iodine vapors).

2,6-Diphenyl-4-(phenyl-o-carboranyl)pyridine (IIa). A 0.55-g (0.001 mole) sample of Ia was triturated in 25% ammonium hydroxide, and the precipitated pyridine was removed by filtration and recrystallized from alcohol—benzene to give a product with mp 192-193°C in quantitative yield. IR spectrum: 2600 (B—H); 1600, 1585, 1560 cm^{-1}. Found: C 67.1; H 6.2; B 24.0; N 3.0%. $C_{25}H_{27}B_{10}N$. Calculated: C 66.8; H 6.0; B 24.0; N 3.1%.

2,6-Di-tert-butyl-4-(methyl-o-carboranyl)pyridine (IIb). A 0.45-g (0.001 mole) sample of Ib was triturated in 25% ammonium hydroxide the solution was decanted, and the viscous residue was triturated with ethanol. The resulting precipitate was removed by filtration and recrystallized from acetonitrile to give a product with mp 121-123°C in 75% yield. IR spectrum: 2600 (B—H); 1590, 1550 cm^{-1}. Found: C 55.1; H 9.2; B 31.4; N 3.9%. $C_{16}H_{33}B_{10}N$. Calculated: C 55.4; H 9.3; B 31.1; N 4.0%.

2,6-Diphenyl-4-(phenyl-1-carboranyl)-1-methylpyridinium Perchlorate (III). A 25% aqueous solution of methylamine was added dropwise to a suspension of 0.55 g (0.001 mole) of Ia in ethanol, during which the pyrylium salt dissolved, and the pyridinium perchlorate precipitated. The precipitate was removed by filtration and recrystallized from acetic anhydride to give a product with mp 258°C (explosively) in 71.5% yield. IR spectrum: 2600 (B—H); 1630, 1570 (pyridinium cation); 1100 cm^{-1} (ClO_4^-). PMR spectrum, δ: 6.70-7.25 (m, 17H, C_6H_5, 3,5-H) and 3.40 ppm (s, 3H, CH_3). Found: B 19.1%. $C_{26}H_{30}B_{10}ClNO_4$. Calculated: B 19.1%.

1,2,6-Triphenyl-4-(phenyl-o-carboranyl)pyridinium Perchlorate (IV). A 0.25-ml sample of aniline was added to a suspension of 0.55 g (0.001 mole) of Ia in glacial acetic acid, and the mixture was heated until the pyrylium salt dissolved. It was then cooled, and the resulting precipitate was removed by filtration and recrystallized from a mixture of glacial acetic acid and acetic anhydride to give a product with mp 236-238°C in quantitative yield. IR spectrum: 2600 (B–H); 1610, 1585, 1540, and 1100 cm^{-1}. Found: B 16.7%. $C_{31}H_{32}B_{10}ClNO_4$. Calculated: B 17.2%.

3,7-Diphenyl-5-(phenyl-o-carboranyl)-4H-1,2-diazepine (VI). A 0.23-ml (0.0025 mole) sample of hydrazine hydrate was added to a suspension of 0.55 g (0.001 mole) of Ia in methanol, during which the pyrylium salt dissolved. The solvent was removed, and the reaction product was extracted from the residue with boiling petroleum ether. Workup gave a product with mp 172-174°C (from alcohol) in 80% yield. IR spectrum: 2600 (B–H); 1620, 1500 cm^{-1}. Found: C 65.0; H 6.4; B 23.3; N 6.1%. $C_{25}H_{28}B_{10}N_2$. Calculated: C 64.6; H 6.1; B 23.3; N 6.0%.

1,3-Diphenyl-5-(phenyl-o-carboranyl)-5-phenacylpyrazoline (V). A) A 0.2-ml sample of phenylhydrazine was added to a suspension of 0.55 g (0.001 mole) of Ia in methanol, and the mixture was refluxed until the pyrylium salt dissolved. The reaction mixture was cooled, the solvent was partially removed, and the precipitate was removed by filtration and recrystallized from acetonitrile to give the product in 90% yield.

B) A 0.2-ml sample of phenylhydrazine was added to a suspension of 0.55 g (0.001 mole) of Ia in glacial acetic acid, during which the pyrylium salt dissolved. The resulting precipitate was removed by filtration and recrystallized from acetonitrile or a mixture of benzene with alcohol to give a product with mp 125-127°C in quantitative yield. IR spectrum: 2600 (B–H); 1680 (C=O); 1600, 1580, 1550, 1520, 1500 cm^{-1}. Found: C 66.7; H 6.3; B 18.8; N 5.3%. $C_{31}H_{34}B_{10}N_2O$. Calculated: C 66.6; H 6.2; B 19.3; N 5.0%.

1-Phenyl-3-tert-butyl-5-(phenyl-o-carboranyl)-5-pivaloylmethylpyrazoline (Vb). A 0.2-ml sample of phenylhydrazine was added dropwise to a suspension of 0.45 g (0.001 mole) of Ib in benzene, during which the pyrylium salt dissolved. The solvent was removed, and the residue was triturated with acetonitrile. The resulting precipitate was removed by filtration and recrystallized from methanol to give a product with mp 118-120°C in 55% yield. IR spectrum: 2600 (B–H); 1700 (C=O); 1600, 1500 cm^{-1}. Found: C 57.4; H 4.3; B 23.6; N 5.8%. $C_{22}H_{40}B_{10}N_2O$. Calculated: C 57.8; H 4.0; B 23.7; N 5.8%.

1-Methoxy-1,5-diphenyl-3-(phenyl-o-carboranyl)pentadien-5-one (VIIa). A) A solution of 0.084 g (0.001 mole) of sodium bicarbonate in water was added to a suspension of 0.55 g (0.001 mole) of Ia in methanol, and the reaction mixture was stirred for several minutes. The resulting precipitate was removed by filtration.

B) A 0.14-ml sample of triethylamine was added to a suspension of 0.55 g (0.001 mole) of Ia in methanol, and the precipitate that formed after brief stirring was removed by filtration.

C) A solution of sodium methoxide prepared from 0.05 g (0.002 mole) of sodium in absolute methanol was added to a suspension of 0.55 g (0.001 mole) of Ia in methanol, during which the pyrylium salt dissolved. The resulting precipitate was removed by filtration.

D) A 0.55-g (0.001 mole) sample of Ia was added to a methanol solution of acetamidine liberated from 0.23 g (2.5 mmole) of its hydrochloride with an equivalent amount of sodium methoxide, during which the pyrylium salt dissolved, and the diketone precipitated.

E) An alcohol solution of sodium methoxide prepared from 0.06 g (2.5 mmole) of sodium was added to a solution of 0.39 g (2.5 mmole) of benzamidine hydrochloride in absolute methanol. The precipitated sodium chloride was removed by filtration, and 0.55 g (0.001 mole) of Ia was added to the solution of the benzamidine base, during which the pyrylium salt dissolved, and a precipitate of the diketone, with mp 167-169°C (from nitromethane), formed.

1-Methoxy-1,5-di-tert-butyl-3-(methyl-o-carboranyl)pentadien-5-one (VIIb). Methanol (5 ml) was added to 0.45 g (0.001 mole) of Ib, and the mixture was stirred, during which the pyrylium salt dissolved, and the desired product, with mp 80-82°C (from methanol), precipitated.

1-Methoxy-1,5-di-tert-butyl-3-(phenyl-o-carboranyl)pentadien-5-one (VIIc). This compound was similarly obtained.

Data on the physicochemical properties of VIIa-c are presented in Table 1.

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KINETICS OF CHLOROMETHYLATION OF BENZO-1,4-DIOXANE

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The chloromethylation of benzo-1,4-dioxane in acetic acid in presence of $SnCl_4$, $SbCl_3$, $ZnCl_2$, and $SbCl_5$ catalysts was investigated. The activation energy of the process was found to be 19.6 kcal/mole. The reaction is zero order in chloride ion and first order in the Hammett acidity function. In excess HCl the reaction is described by a second-order equation. The relative activities of the methyl chlorides in the chloromethylation of benzo-1,4-dioxane were determined.

Benzo-1,4-dioxane derivatives, which are of interest owing to their pharmacological properties [1, 2], can be synthesized by haloalkylation. Chloromethylation, to which a good deal of study has been devoted in the case of aromatic hydrocarbons, has been the subject of relatively little study in the case of compounds of the benzo-1,4-dioxane series [3-8], and it has not yet been evaluated quantitatively. In our communication we present kinetic data on the chloromethylation of benzo-1,4-dioxane in acetic acid in the presence of zinc, tin(IV), antimony(III), and antimony(V) at 50-75°C. A study of the kinetic principles of this reaction confirms its acid-catalytic mechanism

$$CH_2O + H^+ \rightleftharpoons {}^+CH_2OH$$

$$^+CH_2OH + ArH \longrightarrow ArCH_2OH + H^+$$

$$ArCH_2OH + HCl \rightleftharpoons ArCH_2Cl + H_2O$$

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