HETARYLCARBORANES AND THEIR DERIVATIVES (REVIEW)

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Data on the synthesis and properties of new derivatives of the heterocyclic series, viz., hetarylcarboranes, which are heterocycles that contain carborane rings as substituents, are correlated and systematized in the review. Methods for the synthesis of oxygen- and nitrogen-containing heterocycles with a carbonyl substituent are examined. It is emphasized that the preparation of carboranylpyrylium salts and their recyclization have played a decisive role in the successful syntheses of hetarylcarboranes. In the discussion of the reactivities of the hetarylcarboranes special attention was directed to the effect of the carborane ring on the properties of the heterocyclic fragments bonded to it. In conclusion, methods for the synthesis of new hetarylcarboranes are noted, and ideas regarding the prospects for their utilization are expressed.

A voluminous amount of material that contains data on the synthesis, physicochemical properties, structures, and reactivities of heterocycles with various aromatic, heteroaromatic, and heteroorganic substituents has been accumulated thus far. The synthesis and study of the properties of heterocycles, particularly those whose rings are directly bonded to, in addition to alkyl and aryl substituents, more complex substituents such as those containing elements of various groups of the periodic system, have fundamental value. Thus the mutual effect of various fragments of such bi- and polynuclear systems, their competitive reaction, the nature of the chemical bonds, and the possibility of their use as ligands in complexing can be investigated in this case.

Among such compounds, heterocycles that contain carborane and its derivatives as substituents were unknown until recently, whereas boron-containing compounds are extremely interesting in both theoretical [1-3] and practical [4, 5] respects.

Hetarylcarboranes were first synthesized by Zakharkin and co-workers in 1967-1969 [6, 7]. More intensive development of methods for the synthesis of hetarylcarboranes and more intensive study of their properties were begun in the nineteen seventies. The preparation of carboranylpyrylium salts and their recyclization at Rostov State University under the supervision and with the direct participation of Professor G. N. Dorofeenko, to whose illustrious memory the authors dedicate the present review, were of decisive significance for the development of this trend in the chemistry of carboranes.

1. Oxygen-Containing Heterocycles with a Carboranyl Substituent

Methods for the synthesis of carboranyl-4H-pyrans [8-16] and carboranylpyrylium salts [8-15] have been developed, and their properties have been studied.

1.1. Carboranyl-4H-pyrans.

Carbonyl compounds [17-20], γ-pyrones [21, 22], saturated δ-diketones [10, 11, 16, 19, 23, 24], and pyrylium salts [8-15, 24-29] are normally used as the starting substances for the synthesis of substituted 4H-pyrans. It has been shown [11] that the most convenient method for the synthesis of 4H-pyrans of the carborane series (I, II) is alkylation of 4-unsubstituted pyrylium cations with the lithium derivatives of o- and m-carboranes in absolute benzene or in a mixture of absolute benzene with absolute ether [8-10, 14]:

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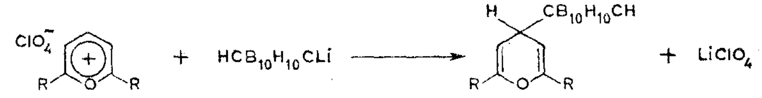
I a-f

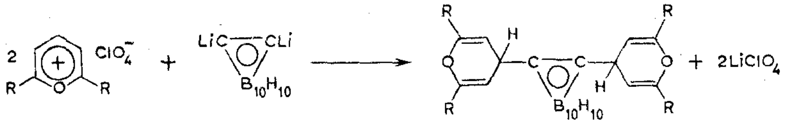
I a $R=H, R'=t\text{-}C_4H_9$; b $R=H, R'=C_6H_5$; c $R=CH_3, R'=t\text{-}C_4H_9$; d $R=C_6H_5, R'=t\text{-}C_4H_9$; e $R=R'=C_6H_5$; f $R=C_6H_5, R'=p\text{-}CH_3OC_6H_4$



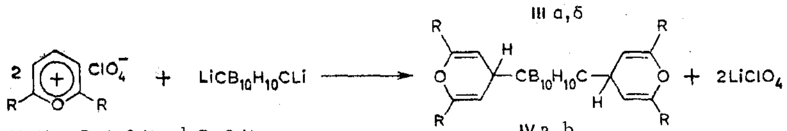
II a,b.

II a $R=t\text{-}C_4H_9$; b $R=C_6H_5$

Bis(o-carboranyl-4H-pyrans) and bis(m-carbornayl-4H-pyrans) (III, IV) were similarly synthesized from the dilution derivatives of o- and m-carboranes and 4-unsubstituted pyrylium salts [12, 13]:



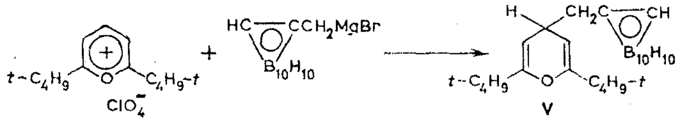
III a,δ



IV a,b

III,IV a $R=t\text{-}C_4H_9$, b $R=C_6H_5$

The reaction of the Grignard reagent obtained on the basis of 1-bromomethyl-o-carborane with 2,6-di-tert-butylpyrylium perchlorate also leads to the formation of the corresponding 4H-pyran V [12, 13]:



V

The principal advantage of this method consists in the possibility of the use of equally readily accessible 4-unsubstituted pyrylium cations [30] and organometallic derivatives of carborane [31-34] as the starting compounds.

The structures of the 4H-pyrans of the carborane series were proved by studies of their IR and PMR spectra [8, 10-14]. An intense band at 1700 cm^{-1}, which is characteristic for the stretching vibrations of the double bonds of the pyran fragment [37], is observed in the IR spectra* of the carboranyl-4H-pyrans. The signal of the proton in the form of a triplet is found at δ 2.77-3.50 ppm in the PMR spectra† of carboranyl-4H-pyrans I-V (in CCl_4). According to the literature data, the γ proton of 2,4,6-triphenyl-4H-pyran appears in the PMR spectrum in the form of a triplet at δ 4.12 ppm (in C_6D_6) [40] and 4.33 ppm (in $CDCl_3$) [41]. The significant shift of the signal of the γ proton in the spectra of carboranyl-4H-pyrans to stronger field (δ 2.77-3.50 ppm) constitutes evidence for the shielding effect of the carborane ring.

The introduction of a carboranyl substituent leads to peculiar properties of the pyran fragment bonded to it. It contrast to many known 4H-pyrans, which are frequently isolated in the form of uncrystallizable oils that are difficult to purify and darken in light [27, 42], carboranyl-4H-pyrans are completely stable and can be stored for a long time without apparent decomposition. They do not undergo ring opening under the influence of HCl and are

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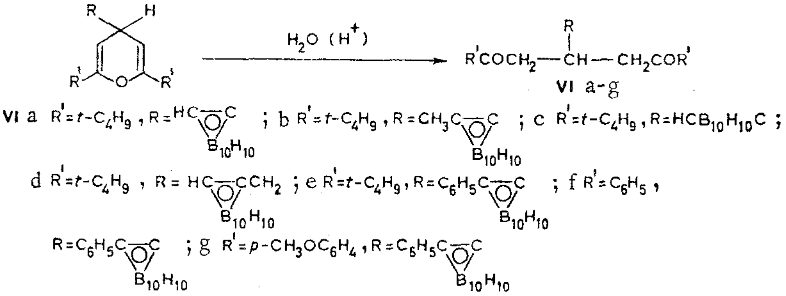
*A strong band at 2600 cm^{-1}, which is due to the stretching vibrations of the B—H bonds of the carborane ring [35, 36], is observed in the IR spectra of compounds of the carborane series.

†It is characteristic for the PMR spectra that the signals of the protons are not resolved at operating frequencies of 60 and 80 MHz [38, 39].

quite resistant to oxidation, in connection with which they undergo dehydroaromatization* with much greater difficulty than ordinary 4H-pyrans [10]. The increased resistance of carboranyl-4H-pyrans to oxidation is confirmed by their polarographic behavior [8]. Thus, whereas 2,6-diphenyl-4H-pyran is oxidized on a stationary platinum microelectrode in acetonitrile with sodium tetrafluoroborate as the inert electrolyte at 1.5 V, 2,6-diphenyl-4-(phenyl-o-carboranyl)-4H-pyran is oxidized at 2.0 V.

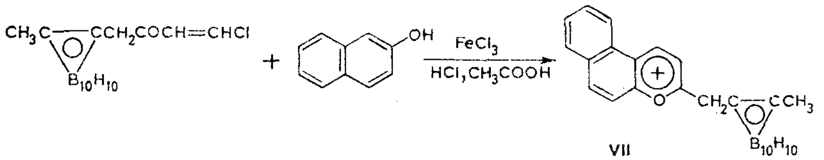
The action of triphenylmethyl perchlorate on 4H-pyrans of the carborane series does not lead to dehydroaromatization; instead, the pyran ring is readily opened to give saturated 1,5-diketones VI [10, 16]. The latter are also formed in the reaction of carboranyl-4H-pyrans with 70% perchloric acid:



Saturated carboranyl δ,δ'-tetraketones are similarly formed from bis(4H-pyrans) by the action of 70% $HClO_4$.

The dehydroaromatization of carboranyl-4H-pyrans, which leads to carboranylpyrylium salts, also proceeds peculiarly [8-15].

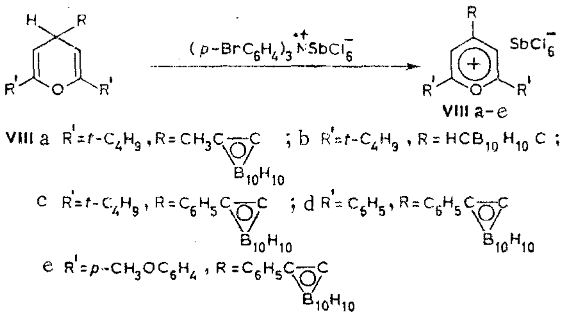
<u>1.2. Carboranylpyrylium Salts.</u> The first carboranylpyrylium derivative (VII) was obtained by Grebennikov and Kazantsev [44] as a result of the reaction of 1-(methyl-o-carboranylmethyl) β-chlorovinyl ketone with β-naphthol in the presence of $FeCl_3$:



VII

1-(Methyl-o-carboranylmethyl) β-chlorovinyl ketone could not be subjected to reaction with other phenols [44]. In VII the naphthopyrylium and carborane groupings are separated by a methylene group, and this hinders the possibility of examination of the mutual effect of the rings.

Pyrylium salts VIII-X, in which the pyrylium cation is bonded directly to the carboranyl icosahedron, were obtained by dehydroaromatization of 4H-pyrans of the carborane series. In particular, a peculiar oxidative dehydrogenation agent, viz., the tris(p-bromophenyl) aminium cation radical, was used for this purpose. In the course of the reaction the components were refluxed until the intensely blue color of the cation radical vanished [8-10]:



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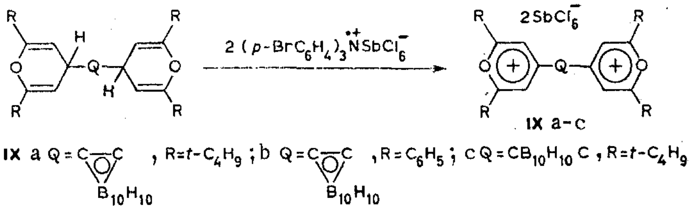
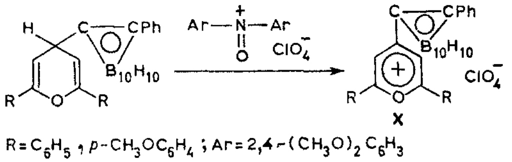
*In particular, in contrast to ordinary 4H-pyrans, which are dehydrogenated via a one-electron oxidation mechanism by the action of quino bromide [42] or via a radical-chain mechanism by the action of CCl_4 [43], carboranyl-4H-pyrans remain unchanged under these conditions.

o- and m-Carboranylbis(pyrylium) bis(hexachloroantimonates) (IX) were obtained on the basis of bis(4H-pyrans) of the o- and m-carborane series as a result of the action of the same dehydrogenating agent [12, 13]:

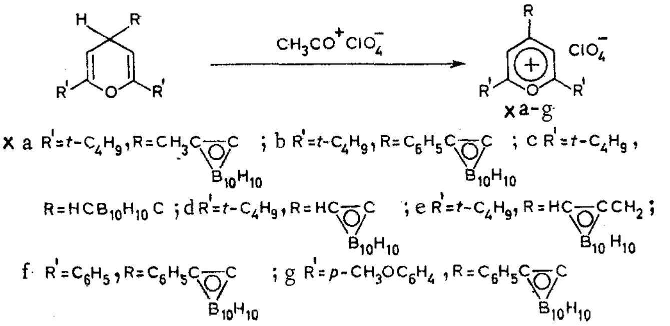


The yields of final salts VIII and IX were quite high.

2,2',4,4'-Tetramethoxydiphenylimmonium perchlorate in acetone has been used as a new dehydrogenating agent in the 4H-pyran series [14, 15]:



However, the dehydroaromatization of 4H-pyrans of the o- and m-carborane series by means of acetyl perchlorate proved to be the best preparative method for the synthesis of carboranylpyrylium perchlorates X (in 50-60% yields) [10, 14]:



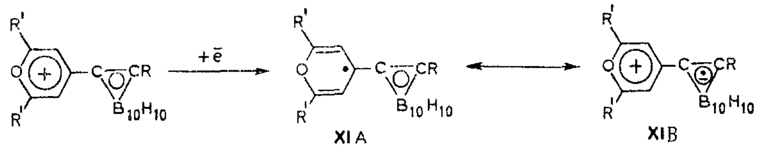
The corresponding carboranylpyrylium chloride is obtained by the action of phosphorus pentachloride on 2,6-di-tert-butyl-4-o-carboranyl-4H-pyran in CCl_4 [10]: 2,6-di-tert-butyl-4-m-carboranylpyrylium chloride cannot be obtained under the indicated conditions, since it decomposes during isolation.

The study of the physicochemical properties and transformations of carboranylpyrylium cations can be carried out most conveniently with the ClO_4^- anion as the gegenion; however, the presence of the $SbCl_6^-$ complex gegenion leads to complications in the course of the reactions and unclear results. Drygina and co-workers [11, 15] were unable to exchange the hexachloroantimonate anion for the perchlorate anion, evidently because of the low solubility of carboranylpyrylium hexachloroantimonates. 2,6-Di-phenyl-4-(phenyl-o-carboranyl)pyrylium iodide was obtained by exchange of ClO_4^- and I^- by means of tetrabutylammonium iodide in acetonitrile [11].

The structures of carboranylpyrylium salts were confirmed by IR and PMR spectroscopy [8, 10-14].

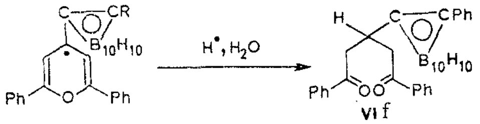
The PMR spectra of carboranylpyrylium salts (in CF_3COOH) do not differ fundamentally from the spectra previously described [45, 46] for 2,4,6-trisubstituted monocyclic pyrylium salts.

Pyranyl radicals XI, which have EPR spectra that are virtually identical to one another, are formed in the reduction of 4-o-carboranyl-pyrylium perchlorates Xa,b,d-g with zinc in acetonitrile or THF (20°C) [14, 15]:

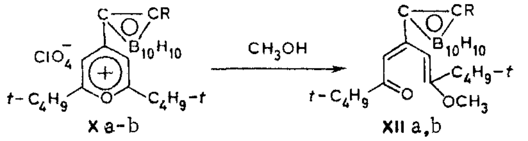


The observed EPR spectra can be interpreted as being the result of interaction of the unpaired electron with six boron atoms (^{11}B, s = 3/2), regardless of the nature of R and R'. The independence of the form of the spectra on the character of R and R' and the high electrophilicity of the carborane ring [47] make it likely that the carboranylpyranyl radicals exist in zwitterion-radical form XIB. The electron-acceptor character of the carborane ring also leads to relative high stabilities of the indicated radicals.

The specific character of the structure of the carboranylpyranyl radicals and the steric hindrance created by the carborane ring hinder the dimerization that is characteristic for pyranyl radicals [48]. Thus the carboranyl radical obtained in the reduction of 2,6-diphenyl-4-(phenyl-o-carboranyl)pyrylium perchlorate does not dimerize but rather is converted in air to 1,3-dibenzoyl-2-(phenyl-o-carboranyl)propane (VIf) [10, 16]:

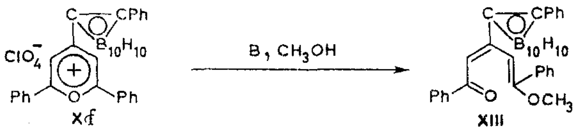


Like other pyrylium salts [49, 50], carboranylpyrylium salts react readily with nucleophilic agents [11, 51]; depending on the nature of the latter, opening or recyclization of the pyrylium ring occurs. Carboranylpyrylium perchlorates Xa,b, which contain tert-butyl groups in the 2 and 6 positions, react directly with methanol as the nucleophilic agent to give methyl ethers of the enol forms of carboranyl-substituted pentadienones (XII):



XII a $R=CH_3$; b $R=C_6H_5$

2,6-Diphenyl-4-(phenyl-o-carboranyl)pyrylium perchlorate (Xf) undergoes ring opening in methanol in the presence of bases (B) to give 1-methoxy-1,5-diphenyl-3-(phenyl-o-carboranyl)pentadienone (XIII):



B Na_2CO_3, CH_3ONa, $(C_2H_5)_3N$, $C_6H_5CH{=}NC_6H_5$, NH_2CONH_2, $(CH_3)_2C{=}NOH$, $(C_6H_5NH)_2C{=}NH$, $H_2NC_6H_4COOC_2H_5$, 5-aminotetrazole

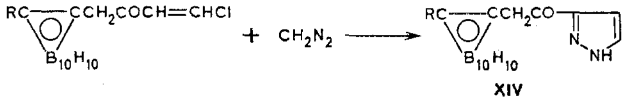
Attack on the pyrylium ring by the methoxide anion is undoubtedly facilitated due to the electron-acceptor effect of the carboranyl substituent. Cations that contain tert-butyl groups in the 2 and 6 positions are particularly activated; they react readily with methanol even at room temperature [51].

Recyclization of the pyrylium cation, which leads to diverse nitrogen heterocycles with a carboranyl substituent in the heterocyclic ring, occurs in the action of nitrogen-containing nucleophilic agents on carboranylpyrylium salts under other conditions.

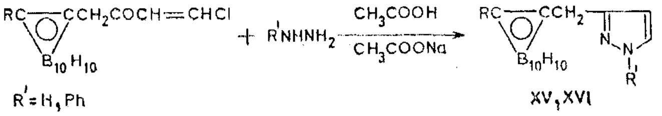
2. Carboranyl Derivatives of Nitrogen-Containing Heterocycles

The presently known nitrogen heterocycles with carboranyl substituents have been obtained chiefly by three methods, viz., by cyclization of some C-substituted derivatives of carborane [6, 7, 52, 53], and by the addition of organometallic derivatives of carboranes to pyridinium salts [55, 56] and other pyridine derivatives [57, 58].

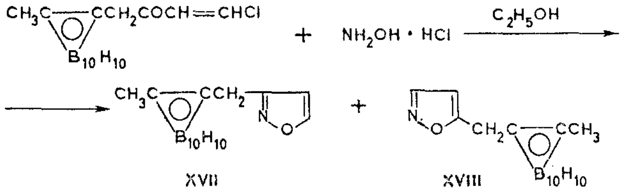
Difficult-to-obtain carboranyl β-chlorovinyl ketones served as the starting substances for the synthesis of carboranyl-substituted nitrogen heterocycles in [6, 7]. Acylpyrazoles XIV are formed smoothly in the reaction of these compounds with diazomethane [6]:



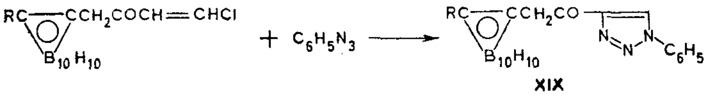
The reaction of carboranyl β-chlorovinyl ketones with hydrazine and phenylhydrazine in acetic acid leads to the corresponding 3-(carboranylmethyl)pyrazoles XV and XVI in good yields [7]:



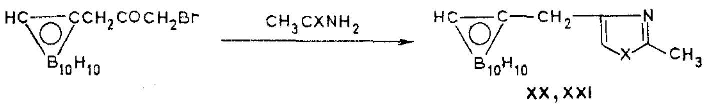
1-(Methyl-o-carboranylmethyl) β-chlorovinyl ketone reacts with hydroxylamine to give a mixture of 3- and 5-(methyl-o-carboranylmethyl)isoxazoles (XVII, XVIII) in 40 and 60% yields, respectively [7]:



1-Phenyl-4-(carboranylacetyl)triazole (XIX) is formed upon prolonged heating of carboranylmethyl β-chlorovinyl ketone with phenyl azide in benzene solution [7]:

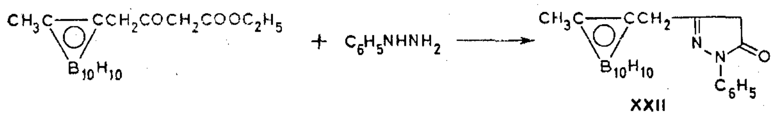


α-Carboranyl-β-bromoacetone undergoes smooth cyclization with thioacetamide to give 2-methyl-4-(carboranylmethyl)thiazole (XX) [52]. A similar reaction with acetamide proceeds with considerably greater difficulty, and 2-methyl-4-(carboranylmethyl)oxazole (XXI) is formed in lower yield [52]:

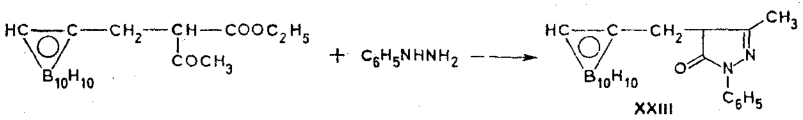


X=O, S

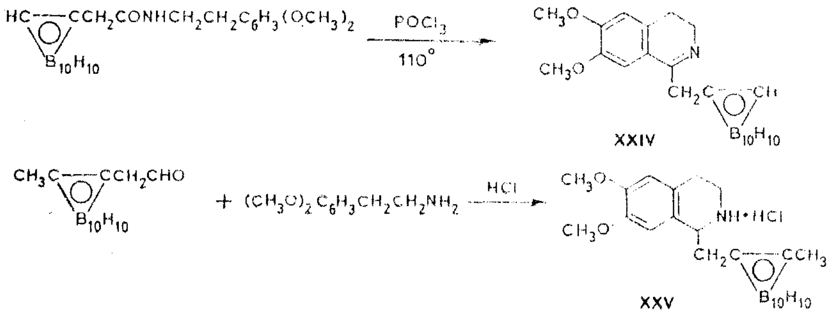
1-Phenyl-3-(methyl-o-carboranylmethyl)pyrazol-5-one (XXII) was obtained from γ-(carboranylmethyl)acetoacetic ester and phenylhydrazine in acetic acid [52]:



1-Phenyl-3-methyl-4-(carboranylmethyl)pyrazol-5-one (XXIII) is formed in the reaction of the corresponding carborane derivative of acetoacetic ester and phenylhydrazine in acetic acid [7]:

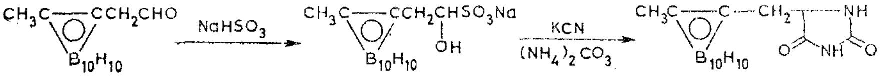


Carboranyl-substituted di- (XXIV) and tetrahydroisoquinolines (XXV) were synthesized [52] by cyclization of carboranylacetic acid β-veratrylethylamide by means of $POCl_3$ by heating in toluene and from methylcarboranylacetaldehyde and β-veratrylethylamine by heating in alcohol saturated with hydrogen chloride:

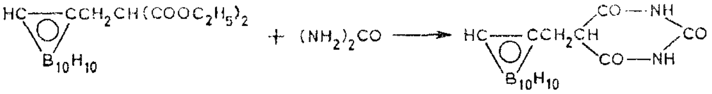

XXIV

XXV

The action of a mixture of KCN and ammonium carbonate on the bisulfite derivative of methylcarboranylacetaldehyde gave 4-(methylcarboranyl)hydantoin (XXVI), which proved to be extremely resistant to acidic hydrolysis [52]:

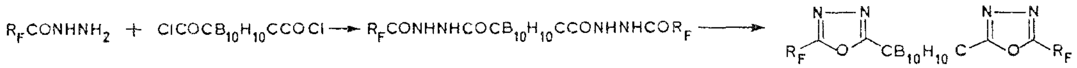

XXVI

5-(Carboranylmethyl)barbituric acid (XXVII) was obtained by the reaction of carboranylmethylmalonic ester and urea [52]:

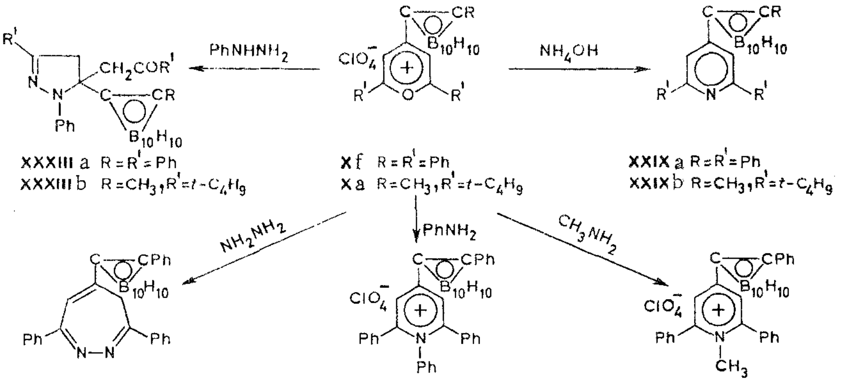

XXVII

5-(Carboranylmethyl)-2,4,6-trichloropyrimidine is formed in low yield when 5-(carboranylmethyl)barbituric acid is heated in a solution of $POCl_3$ with PCl_5 [52].

Carborane-1,7-dicarboxylic acid N,N'-bis(perfluoroalkanoyl)dihydrazides, obtained from perfluoroalkanecarboxylic acid hydrazides and carborane-1,7-dicarboxylic acid dichlorides, undergo intramolecular cyclodehydration to 1,7-bis(2-perfluoroalkyl-1,3,4-oxadiazol-5-yl)carboranes (XXVIII) under the influence of phosphorus pentachloride [53]:


XXVIII

Nitrogen heterocycles with a carboranyl substituent bonded directly to the heterocyclic ring are readily obtained by the action of nitrogen-containing nucleophiles on carboranylpyrylium salts [11, 51, 54]:


XXXIII a R = R' = Ph
XXXIII b R = CH_3, R' = t-C_4H_9
Xf R = R' = Ph
Xa R = CH_3, R' = t-C_4H_9
XXIX a R = R' = Ph
XXIX b R = CH_3, R' = t-C_4H_9

XXXII

XXXI

XXX

The reactions are generally realized at room temperature. The carborane ring, which usually undergoes destruction under the influence of trialkylamines, ammonia, piperidine, and alcoholic alkali, is not affected in the course of the indicated transformations [2].

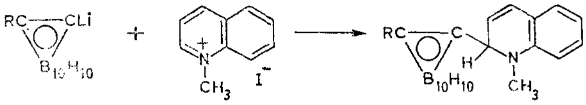
Conversion to the corresponding pyridines is most characteristic for the pyrylium salts. 2,6-Diphenyl-4-(phenyl-o-carboranyl)pyrylium and 2,6-di-tert-butyl-4-(methyl-o-carboranyl) pyrylium perchlorates are readily converted to the corresponding carboranyl-substituted pyridines XXIX in high yields under the influence of ammonium hydroxide. The compounds obtained also serve as characteristic derivatives for the identification of the starting pyrylium salts, inasmuch as carboranylpyrylium perchlorates explode when they are heated.

The action of primary aliphatic and aromatic amines, viz., methylamine and aniline, leads to N-methyl- (XXX) and N-phenylpyridinium (XXXI) perchlorates only when there are phenyl groups in the α positions of the pyrylium ring. The presence of bulky tert-butyl groups in the 2 and 6 positions hinders these transformations.

2,5-Diphenyl-4-(phenyl-o-carboranyl)pyrylium perchlorate behaves like 2,4,6-triarylpyrylium salts [49] in reactions with hydrazine and phenylhydrazine in methanol to give carboranyl derivatives of diazepine (XXXII) and pyrazoline (XXXIIIa). A pyrazoline is also formed even in glacial acetic acid. 2,6-Di-tert-butyl-4-(methyl-o-carboranyl)pyrylium perchlorate gives the corresponding pyrazoline XXXIIIb upon reaction with phenylhydrazine in benzene. These facts made it possible for Drygina and co-workers [11, 51, 54] to conclude that the solvent has a great effect on the course of the reactions.

Syntheses of nitrogen-containing hetarylcarboranes and their derivatives on the basis of organometallic derivatives of the carborane series have been accomplished for six-membered heterocycles that contain one nitrogen atom in the ring.

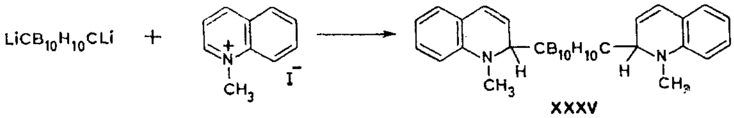
o- and m-Carboranyllithiums react readily with 1-methylquinolinium iodide in ether—benzene to give 1-methyl-2-carboranyl-1,2-dihydroquinolines (XXXIV) [55]:



$R = H, CH_3, C_6H_5$

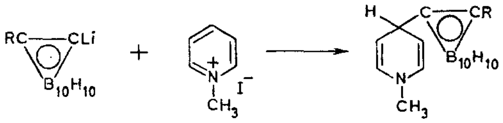
XXXIV

m-Carboranyldilithium reacts similarly with 1-methylisoquinolinium iodide to give bis (1-methyl-1,2-dihydroquinolyl)-m-carborane (XXXV) [55]:



XXXV

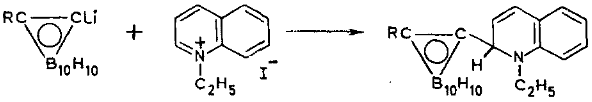
Organometallic compounds generally add to 1-substituted pyridinium salts in the 2 position. Carboranyllithiums add to 1-methylpyridinium iodide in the 4 position to give 1-methyl-4-carboranyl-1,4-dihydropyridine (XXXVI) [55]:



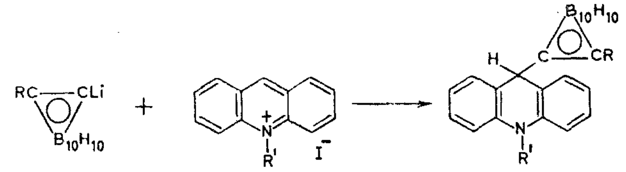
$R = CH_3, C_6H_5$

XXXVI

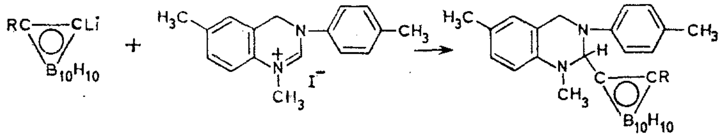
Carboranyllithiums also react readily with 1-ethylquinolinium and 10-methyl(ethyl)acridinium iodides and 6-methyl-3-(p-tolyl)-3,4-dihydroquinazoline methiodide in ether—benzene solution to give the corresponding 1-ethyl-2-carboranyl-1,2-dihydroquinolines (XXXVII), 9-carboranyl-10-methyl(ethyl)-dihydroacridines (XXXVIII), and 1,6-dimethyl-2-carboranyl-3-(p-tolyl)-1,2,3,4-tetrahydroquinazolines (XXXIX) [56]:



XXXVII



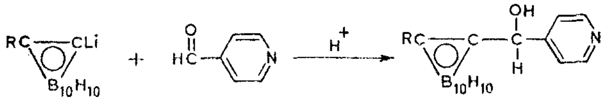
XXXVIII



$R = CH_3, C_6H_5$; $R' = CH_3, C_2H_5$

XXXIX

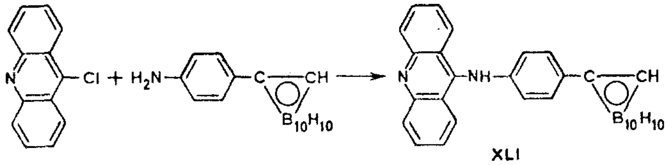
Pyridyl(o-carboranyl)carbinols XL were synthesized from carboranyllithiums and organomagnesium derivatives of o-carborane and α- and γ-formylpyridines [57, 58]:



$R = CH_3, C_6H_5$

XL

It is natural that heterocyclic compounds with carboranyl substituents can also be obtained by introduction of a heteroring in other derivatives of the carborane series. Thus 9-(p-aminophenyl-o-carboranyl)acridine (XLI) was obtained by condensation of 1-(p-aminophenyl)-o-carborane with 9-chloroacridine [59]:



XLI

The structures of the nitrogen-containing carboranyl-substituted heterocycles are confirmed primarily by IR spectroscopy; the PMR spectra have been examined only in a number of cases [51, 55].

Nitrogen-containing heterocycles are included in the compositions of thermally stable azole-carborane polymers [4], among which polyoxadiazoles [60-64], polybenzimidazoles [65], and copolymers of polyoxadiazoles with polytriazoles [66, 67] are known. The corresponding carboranyl polymers [68, 69], which include a natural substance, are formed in the reaction of cellulose iodotosylate and C-phenyl-o-carboranyllithium or o-carboranyl Grignard reagents in ether or THF. Detailed information on polymers based on hetarylcarboranes is contained in a monograph [4] and in the literature cited therein.

CONCLUSIONS

The data presented in this review constitute evidence that although a number of five-membered (isoxazoles, pyrazoles, pyrazolines, pyrazolones, thiazoles, oxazoles, triazoles, and oxadiazoles), six-membered (4H-pyrans, pyrylium salts, pyridines, pyridinium salts, dihydropyridines, dihydroquinolines, tetrahydroquinolines, and tetrahydroquinazolines), and seven-membered (carboranyldiazepine) heterocycles of the carborane series have already been synthesized, hetarylcarboranes and their derivatives still constitute a relatively little-studied class of compounds. This situation is explained by the fact that, for example, the carborane and heterocyclic fragments in five-membered heterocycles are generally bonded through the methylene grouping, in which case their specific mutual effect is significantly weakened. Nevertheless, investigations of the individual properties of heterocycles with a carboranyl substituent in the ring (I-V and X) [10, 11, 14, 51] provide evidence for the peculiar effect of the carborane icosahedron on the heterocyclic fragment bonded directly to it. Thus the reactivities increase markedly in the case of pyrylium cations, and, in contrast to pyrylium salts with other electron-acceptor groupings in the 4 position, in reactions with nucleophilic agents they do not retain their pyrylium structure and are not converted to 4H-pyran derivatives but rather undergo recyclization or ring opening. In addition to this, very little study has been devoted to the properties of the nitrogen-containing fragments of hetarylcarboranes and their derivatives of the XIV-XXXIII [6, 7, 11, 51, 52] and XXXIV-XLI [55, 56] type, and only disparate data involving only its destruction are available regarding the properties of the carborane icosahedron [55, 56].

Fundamental methods for the synthesis of hetarylcarboranes and their derivatives, among which the recyclization of carboranylpyrylium salts occupies a special position, have been well developed thus far. However, these methods have been used only to obtain a limited number of oxygen- and nitrogen-containing heterocycles. Moreover, it is known that pyrylium cations can be successfully converted to phosphorus- [70, 71] and sulfur-containing [72] heterocycles, various azoles [73, 74], etc. There is no doubt that new compounds with unusual properties will be obtained in attempts to extend these reactions to carboranylpyrylium salts. However, judging from the data already available [1-5, 59, 75-79], the prospects for the use of the latter are significant.

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POLYFURYL(ARYL)ALKANES AND THEIR DERIVATIVES. 2.* TRIFURYLALKANES AND MECHANISM OF THEIR FORMATION

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and S. V. Zhuravlev

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Alkylfurans react with carboxylic acid anhydrides and chlorides in benzene in the presence of catalytic amounts of perchloric acid to give trifurylalkanes. The mechanism of the reaction, which is a consecutive process with the successive formation of an acylfuran, an alkyldifurylcarbinol, and a trifurylalkane, is examined. Intermediates, including an alkyldifurylcarbonium perchlorate, were isolated and characterized.

Of the trifurylalkanes, only 1,1,1-tri(5-methyl-2-furyl)ethane, which was isolated by one of us in collaboration with Shapiro [2] from the side products of the acetylation of α-methylfuran by the method in [3], has been described.

We obtained trifurylalkanes I-VIII by the reaction of alkylfurans with acetic anhydride or with caproyl and α-bromopropionyl chlorides in the presence of a catalytic amount of perchloric acid [4]. The most active 2-alkyl- and 2,4-dialkylfurans were used as the starting compounds. Considering the tendency of alkylfurans to undergo self-condensation in the presence of mineral acids, we carried out the reaction in benzene. This makes it possible to carry out the transformation regardless of the nature of the aggregate state of the substances and to obtain trifurylalkanes I and IV-VII in high yields (Tables 1, 2, and 4). The use of any halides leads to partial resinification and a decrease in the yields to 60% (II, III, and VIII). The corresponding 5-alkyl-2-acylfuran, the amount of which depends on the nature of the reagents, their ratio, and the order of mixing, is always formed as a side product.

The electronic spectra of trifurylalkanes I-VIII are similar to the UV spectra of alkylfurans but differ with respect to higher intensities.

The absorption bands of the alkyl substituents (1345-1470 cm^{-1} and characteristic vibrations of the furan ring are the most intense bands in the IR spectra of I-VIII.

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*See [1] for Communication 1.

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