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Boris A. Izmaylov, Valerii A. Vasnev, Galy D. Markova

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On the reactions of haloidmagnesiummethyl-*m*-carboranes

with organoalkoxysilanes and chlorosilanes

Boris A. Izmaylov, Valerii A. Vasnev, Galy D. Markova*

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28

Vavilov Str., Moscow, 119991, Russia

* Corresponding author E-mail address: <u>mgaly@yandex.ru</u> (G.D.Markova)

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ABSTRACT

For the first time an effective method for the preparation of

1-methoxy(dimethyl)silylmethyl-m-carborane and

1,7-bis[chloro(dimethyl)silylmethyl]-*m*-carborane using 1-haloidmagnesiummethyl -*m*-carborane and 1,7-bis[haloidmagnesiummethyl]-*m*-carborane was developed. It has been established that in the course of the reaction of 1-haloidmethyl-*m*carboranes with magnesium both in ether and THF, simultaneously with the formation of 1-haloidmagnesiummethyl-*m*-carborane - the resulting Grignard reagent, proceeds the isomerization of carborane products and their remetallization with the obtained Grignard reagent. This leads to the formation of a complex mixture of products and the decrease in the yield of the resulting Grignard reagent to 43-67%. It has been shown that by using 1-haloidmethyl-*m*-carboranes

substituted in the second carbon atom, for example, 1,7-bis[bromomethyl]-*m*-carborane, in the reactions for obtaining Grignard reagents, it is possible to eliminate the isomerization of carborane products and their remetallization with the target Grignard reagent 1,7-bis[bromomagnesiummethyl]-m-carborane in 90% yield.

Keywords: Grignard reagent; Haloidmagnesiummethyl-*m*-carboranes; Dimethyldiethoxysilane; Dimethyldichlorsilane; Remetallization.

1. Introduction

Earlier disilylmethylcarbosubstituted obtained we monoand o(m)-carboranes by the reaction of mono- and dilithium-o(m)-carboranes with chloromethyl(organo)alkoxysilanes [1,2]. carboranemethyl In containing organosilicone compounds, the Si-CH₂-C_{carb} bond system possesses high thermal stability and resistance to the action of aggressive reagents [1-10]. From synthesized compounds were obtained carboranylmethyl(organo)siloxane and silazane fluids, oils and lubricants [2,4-8], elastomers and vulcanizates [9], thermosetting products for adhesives [8,10,11].

For the synthesis of carboranylmethyl containing organosilicone compounds with $Si-CH_2-C_{carb}$ bond system, the reaction of haloidmagnesiummethyl-*m*-carboranes with organoalkoxysilanes and chlorosilanes is also of interest. Attention to this

reaction is caused by the use in it not only haloidmagnesiummethyl-*m*-carboranes but also common organoalkoxysilanes and chlorosilanes, rather than carbofunctional chloromethyl containing organoalkoxysilanes, which were used in reactions with lithium-*m*-carboranes [1, 2].

2. Results and discussion

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The results of investigation of the reaction of haloidmagnesiummethyl-*m*-carboranes with dimethyldimethoxysilane and dimethyldichlorosilane are represented in this paper. It was found that in a course of the reaction of 1-chloromagnesiummethyl-*m*-carborane with dimethyldimethoxysilane in the solution of diethyl ether a mixture of 66% of 1-methoxy(dimethyl)silylmethyl-*m*-carborane (**I**), 11% of 1-methyl-7-methoxy(dimethyl)silyl-*m*-carborane (**II**), 6% of 1-methoxy(dimethyl)silyl-7-methoxy(dimethyl)silylmethyl-*m*-carborane (**III**) and 17% of 1-methyl-*m*-carborane (**IV**) was formed (**Scheme 1**).



Scheme 1.

Reactions of 1-haloidmagnesiummethyl-*m*-carboranes with dimethyldimethoxysilane in a solution of diethyl ether.

In THF 1-chloromagnesiummethyl-*m*-carborane reacts with dimethyldimethoxysilane and also form the mixture consisting of 45% (**I**), 28% (**II**), 2% (**III**) and 25% (**IV**).

In the reaction of 1-bromomagnesiummethyl-*m*-carborane with dimethyldimethoxysilane both in ether and in THF, mixtures of products, that are close in composition, are formed. So the mixture of products consisting of 35% (**I**),

31% (**II**), 7% (**III**) and 27% (**IV**) is formed in the ether, and in the THF - the mixture of products consisting of 33% (**I**), 30% (**II**), 4% (**III**) and 33% (**IV**).

To facilitate the isolation of the compound (I) from the reaction mixtures, the ability of Si-C_{carb} bond in the compounds (II) and (III) to splitting under the action of nucleophilic and electrophilic reagents was used. For this mixture of products from the reactions of haloidmagnesiummethyl-*m*-carboranes with dimethyldimethoxysilane was treated at room temperature by catalytic amounts of sodium methoxide in methanol solution. In the presence of sodium methoxide, the substance (II) in the mixture is transformed into substance (IV) and substance (III) into substance (I) (Scheme 2). Substances (I) and (IV) were isolated from the new mixture by distillation.

$$I + II + III + IV \xrightarrow{MeONa} II \longrightarrow IV$$

$$MeOH III \longrightarrow I$$

Scheme 2.

The transformation of the compounds in the presence of sodium methoxide.

Substances (I) and (IV) were isolated from the new mixture by distillation. Thus, 1-methoxy(dimetyl)silylmethyl-*m*-carborane (I) was isolated from mixtures obtained from 1-chloromagnesiummethyl-*m*-carborane in ether and THF and treated with sodium methoxide with yield of 60% and 40%, respectively and from mixtures based on 1-bromomagnesiummethyl-*m*-carborane with a yield of 30%, in

both solvents. The formation of silicon-containing products indicates a low selectivity of the reaction of formation of initial Grignard reagents - haloidmagnesiummethyl-*m*-carboranes both in ether and in THF.

Formation of significant amounts of by-products in these reactions is apparently due to the fact that the reactions of the initial 1-haloidmethyl-*m*-carboranes with magnesium both in ether and in THF result in isomerization of starting 1-haloidmethyl-*m*-carboranes, which lead to the formation of by-products.

We suppose that 1-bromomethyl-*m*-carborane reacts with magnesium more readily than 1-chloromethyl-*m*-carborane. Therefore, in the case of the bromo derivative, more carborane anions apparently formed on the magnesium surface, which increases the possibility of interaction between them and explains the formation of more by-products than in the case of a chloroderivative product. It is also possible that in the reaction of 1-bromomethyl-*m*-carborane with magnesium in THF also takes place intermolecular reaction of remetallization of isomerization products with the resulting Grignard reagent. The remetallization reaction is greatly facilitated in the presence of a stronger solvating solvent [**12**], which is THF compared to diethyl ether. Previously, a significant influence of the solvent was shown on the example of formation of *o*-carborane methyl derivatives [**13,14,15**].

It can be assumed that initially from 1-bromomethyl-m-carborane in THF forms target Grignard reagent - 1-bromomagnesiummethyl-m-carborane (V) which

metallizes 1-bromomethyl-*m*-carborane giving 1-methyl-*m*-carborane and 1bromomagnesium-7-bromomethyl-*m*-carborane (**VI**). The latter, upon interaction with magnesium, converts to 1-bromomagnesium-7-bromomagnesium-methyl-*m*carborane (**VII**), which in turn metallizes 1-bromomethyl-*m*-carborane giving 1-bromomagnesium-7-methyl-*m*-carborane

(VIII) (Scheme3):



Scheme 3.

Isomerization of carboranemagnesiumorganic compounds.

It is obvious that similarly in reactions of the types **b**), **c**) and **d**) (Scheme 3) take place the formation of isomerized products by the interaction of 1-

bromomethyl-*m*-carborane with magnesium in diethyl ether, as well as in the reactions of chloromethyl-*m*-carboranes with magnesium diethyl ether and THF.

The reaction with bromine at which 1-methyl-7-bromo-*m*-carborane, 1-bromomethyl-*m*-carborane and 1-bromomethyl-7-bromo-*m*-carborane are formed from compounds (\mathbf{V}) – (\mathbf{VIII}) is a simple and precise determination of the relative amounts of the reaction products of interaction 1-haloidmethyl-*m*-carboranes with magnesium (**Scheme 4**):



Scheme 4.

Bromation of carboranemagnesiumorganic compounds.

These compounds and 1-methyl-*m*-carborane are easily determined by gas-liquid chromatography.

It was found that the relative amounts of compounds (**V-VIII**) and 1-methyl-*m*-carborane vary depending on the reaction conditions: the amounts of magnesium and ether (or THF) and the rate of addition 1-bromomethyl-*m*-carborane to magnesium.

In present work, as a rule, the reaction was carried out at a molar ratio of 1-bromomethyl-*m*-carborane : magnesium, equal to 1:2. The following ratio of reaction products was found: in ether - 36% (**V**), 32% (**VI**), 8% (**VII**) and 24% of 1-methyl-*m*-carborane; in THF - 34% (**V**), 31% (**VI**), 4% (**VII**) and 31% of 1-methyl-*m*-carborane. With a decrease in the amount of magnesium to the ratio 1-haloidmethyl-*m*-carborane : magnesium = 1:1, the amounts of compound **VIII** and 1-methyl-*m*-carborane increase. The amount of 1-methyl-*m*-carborane determined by this method corresponds to the amount of 1-methyl-*m*-carborane which sublimated in vacuum from the reaction mass after removal of ether or THF

We supposed that the use of 1-haloidmethyl-*m*-carboranes substituted at the second carbon atom, for example 1-haloidmethyl-7-methyl-*m*-carborane or 1,7-bis(haloidmethyl)-*m*-carborane, in the reactions for obtaining Grignard reagents, will allow to eliminate the isomerization of carborane products and the reaction of their remetallization and, as a result, increase the yield of Grignard reagent. Indeed, it has been found that the reaction of 1,7-bis(bromomethyl)-*m*-

carborane with magnesium in diethyl ether produces only 1,7-bis(bromomagnesiummethyl)-*m*-carborane in 90% yield. Grignard reagents of this type, reacting with dimethyldimethoxysilane or dimethyldichlorosilane (**Scheme 5**), form the corresponding 1,7-bis[methoxy(dimethyl)silylmethyl]-*m*-carborane (**IX**) and 1,7-bis[chloro(dimethyl)silylmethyl]-*m*-carborane (**X**) in 80% yield:



Scheme 5.

Reaction of bis-Grignard reagents of *m*-carborane with

dimethyldimethoxysilane or dimethyldichlorosilane.

3. Conclusions

Thus, as a result of investigations, it has been found that in the course of the reaction 1-haloidmethyl-*m*-carboranes with magnesium both in ether and THF simultaneously with the formation of 1-haloidmagnesiummethyl-*m*-carborane - the

target Grignard reagent, goes the isomerization of carborane products and their remetallization with the resulting Grignard reagent. This leads to the formation of complex mixture of products and the decrease in the yield of the target Grignard reagent to 35-68%.

It has been found that using 1-haloidmethyl-*m*-carboranes substituted at the second carbon atom, for example 1,7-bis(bromomethyl)-*m*-carborane, in the reactions of obtaining Grignard reagents, it is possible to eliminate the carborane products isomerization and their remetallization with the resulting Grignard reagent and obtain target Grignard reagent - 1,7-bis(bromomagnesiummethyl)-*m*-carborane in ether with 90% yield. It has been shown the possibility of obtaining from Grignard reagent of this type and dimethyldimethoxysilane and also dimethyldichlorosilane, respectively, 1,7-bis[methoxy(dimethyl)silylmethyl]-*m*-carborane (**IX**) and 1,7-bis [chloro(dimethyl)silylmethyl]-*m*-carborane (**X**) in 80% yield.

4. Experimental

4.1. Materials and methods

For syntheses were used: 1-chloromethyl-*m*-carborane, m.p. = 91-92 $^{\circ}$ C (from

hexane); 1-bromomethyl-*m*-carborane, m.p. = $31-32^{\circ}C$ (from hexane);

1,7-bis (bromomethyl)-*m*-carborane, b.p. = 141^{0} C (2.7 gPa); dimethyldimethoxysilane, b.p. = 80^{0} C, n_{d}^{20} = 1.3708; dimethyldichlorosilane; b.p. = $70-71^{0}$ C, n_{d}^{20} = 1.4002. All reactions with carborane derivatives were carried out

in an atmosphere of dry nitrogen. Diethyl ether and THF were absolutized by distillation over LiAlH₄. The molecular weights of compounds (**I**), (**IX**) and (**X**) were determined by cryoscopy in benzene. GLC was carried out on 2 m long columns, filled with 10% silicone elastomer "E-301" on a chromaton in temperature range 150-180^oC (gas-carrier is helium). NMR spectra in CDCl₃ were recorded using Bruker Avance-400 spectrometer with 400.13 MHz working frequency. IR spectra were recorded using "Specord M80" infrared spectrophotometer (Germany) in the frequency range 4000-400 cm⁻¹ on KBr plates.

4.2. Reaction of 1-chloromethyl- and 1-bromomethyl-m-carboranes with magnesium in diethyl ether

1.4 g of magnesium filings under a 50 ml layer of absolute diethyl ether was activated by several drops of 1,2-dibromoethane and 7.7 g (0.039 mol) of 1-chloromethyl-*m*-carborane in 50 ml of absolute diethyl ether was then added. The mixture was refluxed for 1 h. The completion of the reaction was determined by GLC method after hydrolysis of the sample from the reaction mixture. Then the solution of 1-chloromagnesiummethyl-*m*-carborane was filtered off from the magnesium excess and introduced into the reaction. An aliquot part of this solution was added with stirring at -30^oC to a solution of dry Br₂ taken with 50% excess in hexane distilled over LiAlH₄. Then solvent with excess of Br₂ was removed in

vacuum. The residue, according to GLC, consisted of 17% of 1-methyl-*m*-carborane, 11.7% of 1-bromo-7-methyl-*m*-carborane, 67% of 1-bromomethyl-*m*-carborane and 4% of 1-bromo-7-bromomethyl-*m*-carborane.

Similarly, the reaction of 1-bromomethyl-*m*-carborane with magnesium in diethyl ether was carried out. An aliquot part of the Grignard reagent was treated with Br₂ in hexane to obtain a product mixture which, according to GLC, consisted of: 25% 1-methyl-*m*-carborane (**IV**), 36% 1-bromomethyl-*m*-carborane (**V**), 33% 1-bromo-7-methyl-*m*-carborane (**VIII**) and 6% 1-bromo-7-bromomethyl-*m*-carborane (**VII**) (see Scheme 3).

4.3. *Reactionm of 1-bromomethyl-m-carborane with magnesium in THF* The reaction of 1-bromomethyl-*m*-carborane with magnesium in THF was carried out similarly, as in diethyl ether. After treatment of aliquot part of the Grignard reagent with Br₂ in hexane, a mixture of products which consisted, according to GLC, of 33% 1-methyl-*m*-carborane (**IV**), 31% 1-methyl-7-bromo-*m*-carborane (**VIII**), 34 % 1-bromomethyl-*m*-carborane (**V**) and 2% 1-bromo-7-bromomethyl-*m*-carborane (**VIII**), was obtained (see **Scheme 3**).

4.4. Reaction of 1,7-bis(bromomethyl)-m-carborane with magnesium in diethyl ether

2.8 g of magnesium filings under a 100 ml layer of absolute diethyl ether was activated by several drops of 1,2-dibromoethane and 6.6 g (0.02 mol) of 1,7bis(bromomethyl)-*m*-carborane in 50 ml of absolute diethyl ether was then added. The mixture was refluxed for 1 h. The completion of the reaction was determined by GLC method after hydrolysis of the sample from the reaction mixture. Then the solution of 1,7-bis(bromomagnesium)-*m*-carborane was filtered off from the magnesium excess and introduced into the reaction. An aliquot part of Grignard reagent was treated with Br_2 in hexane and a mixture of products was obtained which contained, according to GLC, 90% of 1,7-bis(bromomethyl)-*m*-carborane.

4.5. Reactions of 1-chloromagnesiummethyl- and 1-bromomagnesiummethyl-m-carboranes with dimethyldimethoxysilane in diethyl ether

10.85 g (0.05 mol) of 1-chloromagnesiummethyl-*m*-carborane in 70 ml of absolute diethyl ether was added dropwise with stirring to 12 g (0.1 mol) of dimethyldimethoxysilane in 70 ml of absolute diethyl ether. The mixture was refluxed for 3 h and cooled. Then 3 ml of 1% sodium methoxide solution in methanol was added, the mixture was refluxed with stirring for 3 h, ether and an excess of dimethyldimethoxysilane were distilled off on a rotary evaporator, and 12.3 g of the mixture was obtained. 1-methyl-m-carborane (**IV**) was distilled from mixture in vacuum and 7.4 g (60%) of 1-methoxy(dimethyl)silylmethyl-*m*-carborane (**I**) was obtained in the residue. B.p.= $115-117^{0}$ C (133 Pa), m.p.= 120-

121^oC (from hexane), n_D^{20} = 1.5160. Found (%): C, 29.70; H, 9.11; B, 44.0; Si, 11.80. M_n 245. For C₆H₂₂SiB₁₀O requires (%): C, 29.24; H, 8.99; B, 43.86; Si, 11.40. M_n=246. IR (Λ , cm⁻¹): 2600 (B-H), 2980 and 2900 (Si-CH₂). ¹H NMR (CDCl₃, ppm): 0.27 (6H, s,2CH₃), 1.70 (2H, s CH₂), 3.00 (1H, s, CH_{carb.}), 3.55 (3H, s, OCH₃).

4.6. Reaction 1-chloromagnesiummethyl-m-carborane with dimethyldimethoxysilane in THF

The reaction was carried out similarly to mode 3.3. From 10.5 g (0.05 mol) of Grignard reagent and 12 g (0.1 mol) of dimethyldimethoxysilane 4.9 g (40%) of compound (\mathbf{I}) was obtained.

4.7. Reaction of 1-bromomagnesiummethyl-m-carborane with dimethyldimethoxysilane in diethyl ether and THF

The reaction of 1-bromomagnesiummethyl-m-carborane with dimethyldimethoxysilane in diethyl ether and THF was carried out similarly to mode 3.3. From 13 g (0.05 mol) of Grignard reagent and 12 g (0.1 mol) of dimethyldimethoxysilane both in diethyl ether and THF 3.7 g (30%) of compoud **I** was obtained.

4.8. Reaction of 1,7-bis(bromomagnesiummethyl)-m-carborane with dimethyldimethoxysilane

9.5 g (0.025 mol) of 1,7-bis(bromomagnesiummethyl)-*m*-carborane in 70 ml of absolute diethyl ether was added dropwise with stirring to 12 g (0.1 mol) of dimethyldimethoxysilane in 70 ml of absolute diethyl ether. The mixture was refluxed for 3 h and cooled. The mixture was refluxed for 5 h. Diethyl ether and an excess of dimethyldimethoxysilane were distilled off on a rotary evaporator and 8.8 g of mixture was obtained. Then volatile products were distilled off in vacuum and 7 g (80%) of 1,7-bis[methoxy(dimethyl)silylmethyl]-m-carborane (**IX**) was obtained. B.p.= 168-170^oC (133 Pa), $n_D^{20} = 1.5105$. Found (%): C, 35.00; H, 9.18; B, 31.90; Si, 16.31. M_n=346. For C₁₀H₃₂Si₂B₁₀O₂ requires (%): C, 34.45; H, 9.25; B, 31.0; Si, 16.11. M_n=348. IR (λ , cm⁻¹): 2600 (B-H), 2980 and 2900 (Si-CH₂). ¹H NMR (CDCl₃ ppm): 0.32 (12H, s, 4CH₃), 1.70 (4H, s, 2CH₂), 3.59 (6H, s, 2OCH₃).

4.9. Reaction of 1,7-bis(bromomagnesiummethyl)-m-carborane with dimethyldichlorosilane

The reaction of dimethyldichlorosilane (12.9 g, 0.1 mol) with 1,7bis(bromomagnesiummethyl)-m-carborane (9.5 г, 0.025 mol) was carried out

similarly to mode 3.7. Yield of compound (X) is 80%. B.p.= 152-154 (133 Pa),

n_D²⁰=1.534. Found (%): C, 27.20; H, 7.28; Si, 15.20; B, 29.20; Cl, 19.18. M_n=355. For C₈H₂₆Si₂B₁₀Cl₂ requires (%): C, 26.27; H, 7.33; Si, 15.71; B, 30.23; Cl, 19.85.

M_n=357. IR (*λ*, cm⁻¹): 2600 (B-H), 2980 and 2900 (Si-CH₂). ¹H NMR (CDCl₃, ppm): 0.48 (12H, s, 4CH₃), 1.30 (4H, s, 2CH₂).

4.10. Preparation of starting haloidmethyl-m-carboranes

1-Chloromethyl-*m*-carborane (**XI**) and 1-bromomethyl-*m*-carborane (**XII**) can't be obtained by thermal isomerization of the corresponding 1-haloidmethyl-*o*carboranes, since the migration of the halogen atom to the boron atoms of carborane nucleus occurs upon heating [**16**]. Their synthesis was carried out in the following way. In the reaction of paraform with 1-lithium-*m*-carborane, which was prepared by metallization of *m*-carborane with butyl lithium at a ratio of 1:1 in ether, a mixture of 1-hydroxymethyl- (**XIII**) and 1,7-dioxymethyl-*m*-carborane (**XIV**) in ratio of 1:1 was obtained (**Scheme 6**).



Scheme 6.

Preparation of mixture of 1-oxymethyl- and 1,7-dioxymethyl-*m*-carborane in the ratio 1:1 in the process of metallization of *m*-carborane with butyllithium.

4.10.1. Preparation of 1-oxymethyl-m-carborane (XIII)

To a solution of lithium-m-carborane (from 10 g of *m*-carborane and 0.007 mol of C₄H₉Li) in a mixture of 30 ml of ether and 50 ml of benzene, 3 g of paraform were added in small portions with stirring. The mixture was refluxed for 2 h. After usual treatment the reaction product was chromatographed on a column with Al₂O₃ (eluent – chloroform) to give 4.2 g (35%) of 1-oxymethyl-*m*-carborane (**XHI**) with m.p. = 214-215^oC (from hexane). Found, (%): C, 20.68; H 7.83; B 61.48. For C₃H₁₄B₁₀O, requires, %: C: C 20.68; H 8.10; B 62.04. Then column was washed with methanol to give 4.3 g (30%) of 1,7-bis(oxymethyl)-m-carborane (**XIV**), m.p. = 193-195^oC (from toluene). According to the literary data [**3**] m. p. = 194-196^oC.

It turned out that compound (**XIII**), unlike 1-hydroxymethyl-*o*-carborane [17] and primary alcohols, reacts with PCl_5 to form substance (**XI**) and *m*-carboranylmethyl ester of phosphoric acid (**XV**):



Scheme 7.

Reaction of 1-oxymethyl-m-carborane with PCl₅.

The chloro-derivative (**XI**) is not formed from the alcohol (**XIII**) under the action of $SOCl_2$ in the presence or absence of pyridine. Under the action of PBr₅ on

alcohols (**XIII**) and (**XIV**) there is no exchange of OH groups with a bromine atom but phosphoric esters are formed. Compound (**XII**) was obtained from alcohol (**XIII**) by the action of $(C_6H_5)_3PBr_2$ (**Scheme 8**):



Synthesis of 1-bromomethyl-m-carborane.

Similarly, from the alcohol (XIV) was obtained 1,7-bis(bromomethyl)-m-

carborane (XVI) (Scheme 9):



Scheme 9.

Synthesis of 1,7-bis(bromomethyl)-*m*-carborane.

4.10.2. Preparation of 1-chloromethyl-m-carborane (XI) [18]

To 9.5 g of PCl₃ in 3 ml of absolute benzene was added with stirring a solution of 5 g of 1-hydroxymethyl-*m*-carborane in 25 ml of absolute benzene. The mixture was boiled until HCl removal stopped (2 h), treated with water, extracted with ether and then ether was distilled off. The obtained residue was chromatographed on a column with Al₂O₃ (eluent-petroleum ether with b.p. = 40-70^oC) and 1.25 g (92%) of product (**XI**) was obtained, m.p. = 91-92^oC (from hexane). Found (%): C, 18.82; H 6.48; B 56.32. For C₃H₁₃B₁₀Cl, requires, %: C: C 18.70; H 6.80; B 56.11. Then column was washed with chloroform to give 3.65 g (90%) of *m*-carboranylmethyl ester of phosphoric acid (**XV**), m.p. = 246-247^oC (from hexane). Found (%): C 19.27; H 7.05; B 57.5; P 5.63. For C₉H₃₉B₃₀O₄P, requires, %: C 19.07; H 6.94; B 57.29; P 5.46.

4.10.3. Preparation of 1-bromomethyl-m-carborame (XII) [18]

The solution of 1.45 g of Br₂ in 5 ml of absolute benzene was added to a solution of 1.0 g of 1-hydroxymethyl-*m*-carborane and 2.1 g of $P(C_6P_5)_3$ in 15 ml of absolute benzene at room temperature with stirring. The mixture was refluxed for 2 h, washed with water, dried over Na₂SO₄ and solvent was distilled off. The obtained residue was chromatographed on a column with Al₂O₃ (eluent-petroleum ether with b.p. = 40-70^oC) and 1.3 g (95%) of product (**XII**) was obtained, m.p. = $31-32^{o}C$ (from hexane). Found (%): C 15.19; H 5.92; B 32.63. For C₃H₁₃B₁₀Br₂, requires, %: C 14.55; H 4.27; B 32.75.

4.10.4. Preparation of 1,7-(dibromomethyl)-m-carborane (XVI) [18]

1,7- (dibromomethyl)-m-carborane (XVI) was prepared similarly to mode 3.10.2 from 3.75 g of 1,7-dioxymethyl-*m*-carborane (XIV) [19], 12.6 g of P(C₆P₅) and 8.7 g of Br₂ in 100 ml of absolute benzene. Yield of product (XIV): 5.3 g (87.5%), b.p. ./s.c Refr = 141^oC (2.7 gPa). Found,% C 14.93; H, 4.32; Br, 32.75. Calculated for

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