PREPARATION OF 9-VINYL- AND 9-ETHYNYL-o- AND m-CARBORANES

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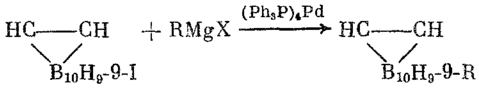
We have already proposed a simple method for preparing 9-alkyl- and 9-aryl-o- and m-carboranes by the reaction of 9-iodo-o- and m-carboranes with organomagnesium compounds, catalyzed by Pd complexes [1, 2]. In the present work, this method is applied to the synthesis of previously unknown 9-vinyl- and 9-ethynyl-o- and m-carboranes from 9-iodo-o- and m-carboranes and the corresponding vinyl- and ethynylmagnesium halides, according to the scheme



(I)—(V)

R = $CH_2{=}CH$ (I), $CH_2{=}CHC{\equiv}C$ (II), $n\text{-}BuC{\equiv}C$ (III), $PhC{\equiv}C$ (IV), $Me_3SiC{\equiv}C$ (V)

$$m\text{-}HCB_{10}H_9(9\text{-}I)CH + RMgX \xrightarrow{(Ph_3P)_4Pd} \underset{(VI)-(X)}{m\text{-}HCB_{10}H_9(9\text{-}R)CH}$$

R = $CH_2{=}CH$ (VI), $CH_2{=}CHC{\equiv}C$ (VII), $n\text{-}BuC{\equiv}C$ (VIII), $PhC{\equiv}C$ (IX), $Me_3SiC{\equiv}C$ (X).

TABLE 1. Reaction Conditions, Yields, Physical Constants, and Data of Elemental Analysis of 9-Vinyl- and 9-Ethynyl-o- and m-Carboranes

Compound	Duration of reaction, h	Yield, g/%	mp, °C (solvent)	Empirical formula	Found/calc., % C	H	B
(I)	40	1,20/71	52–53 (pentane)	$C_4H_{14}B_{10}$	28,59/28,22	8,43/8,29	63,70/63,49
(II)	30	1,50/77	131–133 (hexane)	$C_6H_{14}B_{10}$	36,83/37,09	7,40/7,26	56,10/55,65
(III)	20	2,0/89	44–45 (pentane)	$C_8H_{20}B_{10}$	42,84/42,83	8,93/8,98	48,21/48,19
(IV)	40	2,2/90	120–121 (hexane)	$C_{10}H_{16}B_{10}$	–	–	43,74/44,24
(V) *	17	2,0/85	107–108 (pentane)	$C_7H_{20}B_{10}Si$	35,13/34,97	8,55/8,39	44,94/44,96
(VI)	40	1,50/88	36–37 (pentane)	$C_4H_{14}B_{10}$	27,99/28,22	8,03/8,29	63,57/63,49
(VII)	30	1,60/82	85–87 (pentane)	$C_6H_{14}B_{10}$	37,50/37,09	7,20/7,26	55,30/55,65
(VIII)	20	1,85/82	bp 114–115 (1 mm)	$C_8H_{20}B_{10}$	–	–	47,91/48,19
(IX)	40	1,1/90	bp 150 (1 mm)	$C_{10}H_{16}B_{10}$	49,45/49,16	6,56/6,60	44,22/44,24
(X) †	17	2,1/87	58–59 (pentane)	$C_7H_{20}B_{10}$	35,15/34,97	8,48/8,39	44,80/44,96
(XI)	30	2,0/79	78–79 (pentane)	$C_{12}H_{20}B_{10}$	52,86/52,91	7,88/7,40	39,61/39,69

*Found: Si 11.50%. Calculated: Si 11.68%.
†Found: Si 11.45%.

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TABLE 2. IR Spectra of 9-Vinyl- and 9-Ethynyl-o- and m-Carboranes*

Compound	Frequencies of stretching vibrations (ν, cm^{-1})
(I)	1610 w (C=C), 3080 s (=CH$_2$), 3035 w (=CH–), 980 m (ρ=CH–), 900 m (ρ=CH$_2$), 1410 m (δ=CH$_2$)
(II)†	2165 m (C≡C), 1660 s (C=C), 3065 v.s (=CH$_2$), 3020 m (=CH–), 980 s (ρ =CH–), 930 s (ρ =CH$_2$), 1415 s (δ =CH$_2$), 1290 m (δ =CH–)
(III)	2180 s (C≡C)
(IV)	2180 m (C≡C), 3050 (CH Ph), 1450 m, 1490 m, 1580 w and 1595 m (C–C Ph), 690 m and 760 s (ρ CH Ph)
(V)	2135 m (C≡C)
(VI)	1610 w (C=C), 3070 s (=CH$_2$), 3040 w (=CH–), 980 m (ρ=CH–), 900 m (ρ =CH$_2$), 1410 m (δ =CH$_2$), 1290 w (δ =CH–)
(VII)	2180 m (C≡C), 1605 s (C=C), 3070 v.s (=CH$_2$), 3025 m (=CH–), 985 v.s (ρ =CH–), 935 v.s (ρ =CH$_2$), 1420 s (δ =CH$_2$), 1300 w (δ =CH–)
(VIII)	2190 s (C≡C)
(IX)	2160 m (C≡C), 3060 s (CH Ph), 1450 m, 1490 m, 1580 w and 1600 m (C–C Ph), 690 s and 760 s (δ CH Ph)
(X)	2135 m (C≡C)
(XII)	2070 m (C≡C), 3290 s (≡CH)
(XIII)	2065 m (C≡C), 3285 s (≡CH)

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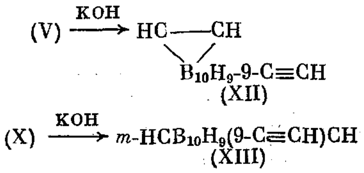
*Solid compounds (I)-(VII), (X), (XII), and (XIII) were pressed into tablets with KBr; the liquid compounds (VIII) and (IX) were measured in a thin layer. In the IR spectra of all the compounds there are bands of stretching vibrations of the BH and CH groups of the carborane ring at 2600 and 3070 cm^{-1}, respectively.

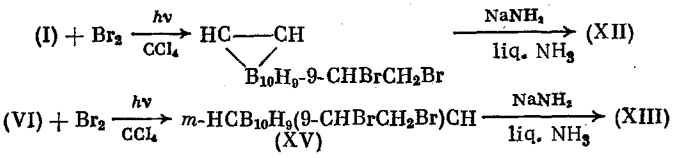
†In the Raman spectrum of (II) there are bands of stretching vibrations of the C≡C bond of the disubstituted acetylene at 2170 cm^{-1} and stretching vibrations of the C=C bond at 1600 cm^{-1}.

The reaction was carried out at 60°C for vinylmagnesium halides in a THF-dioxane mixture, and for ethynylmagnesium halide in an ether–dioxane mixture. Among the complexes studied as catalysts – $(Ph_3P)_2PdCl_2$ and $(Ph_3P_4Pd$ – the latter is more active and is used in an amount of 2 mole% with respect to iodocarborane. 1,2-Dimethyl-9-phenylethynyl-o-carborane (XI) was obtained by this method from 1,2-dimethyl-9-iodo-o-carborane. The yields of products (I)-(XI) are 71-90% (Table 1), i.e., the proposed method is fully suitable for preparative purposes.

By the action of alcoholic alkali on (V) and (X), the previously unknown 9-ethynyl-o- (XII) and 9-ethynyl-m-carboranes (XIII), respectively, were synthesized. These were also

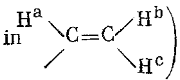
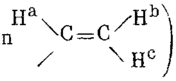


obtained from (I) and (VI) according to the following scheme:



Bromination of (I) and (VI) proceeds readily under UV irradiation in CCl_4. Compounds (XII) and (XIII) are smoothly obtained by reaction of dibromides (XIV) and (XV) with $NaNH_2$ in liquid NH_3.

TABLE 3. PMR Spectra of 9-Vinyl- and 9-Ethynyl-o- and m-Carboranes*

Compound	^1H (δ, ppm, TMS)	J, Hz
(I)	3.37 br.s (1H) and 3.44 br.s (1H) (two equivalent CH of carborane ring), 5.83 m (1H, $-CH=$), 5.19 and 5.28 unresolved m with two max (2H, $=CH_2$)	12 (cis-CH=CH) 17 (trans-CH=CH)
(II)	3.43 br.s (1H) and 3.52 br.s (1H) (two equivalent CH of carborane ring), 5.71 m (1H, H^a in ), 5,37 m (1H, H^B), 5,51 m (1H, H^c)	10,7 (cis-H^aH^b), 17,4 (trans-H^aH^c) 3 (gem-H^bH^c)
(III)	3.48 br.s (1H) and 3.58 br.s (1H) (two equivalent CH of carborane ring), 0.91 t (3H, Me), 1.41 m (4H, CH_2-CH_2), 2.09 t (2H, BCH_2)	6,5 ($MeCH_2$) 6,5 (BCHMe)
(IV)	3.25 br.s (1H) and 3.37 br.s (1H) (two equivalent CH of carborane ring), 7.20 and 7.31 m with two max (5H, Ph)	
(VI)	2.85 br.s (2H, CH of carborane ring), 5.93 m (1H, $-CH=$), 5.38 and 5.46 (2H), unresolved multiplet with two max ($=CH_2$)	12 (cis -CH=CH) 19 (trans-CH=CH)
(VII)	2.87 br.s (2H, CH of carborane ring), 5.74 m (1H, H^a in ) 5,38 m (1H, H^b), 5,55 (1H, H^c)	10,7 (cis -H^aH^b), 17,4 (trans -H^aH^c) 3 (gem-H^bH^c)
(VIII)	2.90 br.s (2H, CH of carborane ring), 0.92 t (3H, Me), 1.44 m (4H, CH_2CH_2), 2.13 t (2H, BCH_2)	6,8 ($MeCH_2$) 6,5 (BCHMe)
(IX)	2.85 br.s (2H, CH of carborane ring), 7.20, 7.37 m with two max (5H, Ph)	
(XI)	2.02 s (3H, Me), 7.16 and 7.30 m with two max (5H, Ph)	
(XI)	2.10 s (1H, ≡CH), 3.35 br.s (1H), 3.45 br.s (1H) (two nonequivalent CH of carborane ring)	
(XIII)	2.02 s (1H, ≡CH), 2.89 br.s (2H) (CH of carborane ring)	

*For 15-20% solutions in CCl_4, internal standard — HMDS.

The structure of (I)-(XIII) was confirmed in IR, Raman (Table 2), and PMR spectra (Table 3).

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer, the Raman spectra on a Ramanor HY2F instrument at an excitation of the 5145 Å line by an argon laser, and the PMR spectra were run on a Bruker WP-200SY spectrometer. The course of the reaction and the individuality of the compounds were controlled by TLC on Silufol, and also by GLC on an LKhM 8MD chromatograph, using a katharometer detector (a 2 m × 3 mm column, filled with 10% SKTFT-50Kh, temperature 180-250°C, flow rate of carrier gas helium 80 ml/min). The solvents (ether, THF) were made absolute by distillation over benzophenone ketyl in a N_2 atmosphere. The yields, physical constants, and data of the elemental analysis of the compounds are listed in Table 1. The IR spectra are presented in Table 2, and the PMR spectra are given in Table 3.

9-Vinyl-o- and m-carboranes (I), (II). A mixture of a THF solution of 27.3 ml (30 mmoles) of CH_2=CHMgBr (concentration 1.10 M), 2.70 g (10 mmoles) of 9-I-o- or 9-I-m-carborane, and 0.23 g (0.2 mole) of $(Ph_3P)_4Pd$ in 100 ml of absolute dioxane was heated for 40 h at 60°C, with stirring, in a N_2 atmosphere (up to the disappearance of iodocarborane in the reaction mixture, according to GLC). The contents were poured into a ∿18% solution of HCl, the mixture was extracted by ether, washed with water, and dried over $MgSO_4$. The solvents were distilled and the residue was chromatographed on a column with silica gel L 40-100 μm, using a 5:95 benzene-petroleum ether (bp 40-70°C) mixture as eluent.

Acetylenic Derivatives of 9-o- and 9-m-Carboranes (II)-(V), (VII)-(X). General Procedure. A 30-mmole portion (17.2 ml of an ether solution at a concentration of 1.74 M) of EtMgBr was added, in a N_2 atmosphere, to a solution of 30 mmoles of RC≡CH (R = CH_2=CH, n-Bu, Ph, Me_3Si) in 50 ml of absolute dioxane. The mixture was heated for 1 h at 40°C and cooled. To the solution of RC≡CMgBr obtained, 2.7 g (10 mmoles) of 9-I-o- or 9-I-m-carborane, 0.23 g (0.2 mole) of $(Ph_3P)_4Pd$ in 100 ml and absolute dioxane were added. The mixture was heated at 60°C, with stirring, for the time indicated in Table 1 (up to the disappearance of iodocarborane, controlled by GLC). The contents were poured into an ∿18% solution of HCl, extracted by ether, washed with water, and dried over $MgSO_4$. The solvents were distilled in vacuo, and the residue was chromatographed on a column with silica gel L 40-100 µm, using a benzene—petroleum ether (bp 40-70°C) mixture as eluent.

Compound (XI) was obtained in a similar way.

9-(1',2'-Dibromoethyl)-o-carborane (XIV). A 1.18-g portion of Br_2 was added to a solution of 1.26 g (7.4 mmoles) of 9-vinyl-o-carborane in 10 ml of CCl_4. The mixture was stirred, held for 1 h under UV irradiation from a PRK-4 lamp, placed at a distance of 25 cm, to complete disappearance of vinylcarborane (TLC). The reaction product was washed with a Na_2SO_3 solution, water, and dried over $MgSO_4$. The solvents were distilled, and the residue was recrystallized. Yield, 1.50 g (61%), mp 93-95°C (hexane). Found: C 14.51; H 4.25; Br 49.19%. $C_4H_{14}B_{10}Br_2$. Calculated: C 14.55; H 4.28; Br 48.12%.

9-(1',2'-Dibromomethyl)-m-carborane (XV). This compound was obtained in the same way and from the same amounts of starting materials. Yield, 1.7 g (70%), mp 52-53°C (hexane). Found: C 14.80; H 4.27; B 32.59; Br 48.59%. $C_4H_{14}B_{10}Br_2$. Calculated: C 14.55; H 4.28; B 32.75; Br 48.12%.

9-Ethynyl-o-carborane (XII). a) Preparation from (V). A 1.27-g portion (5.3 mmoles) of 9-trimethylsilyethynyl-o-carborane was dissolved in 100 ml of 1% KOH solution in MeOH, and the mixture was left to stand for 2 h at 20°C. The reaction mixture was poured into water, extracted by ether, and washed with water, and the ether extracts were dried over $MgSO_4$. The solvent was distilled in vacuo, and the residue was sublimed in vacuo, and recrystallized. Yield, 0.70 g (76%), mp 146-147°C (pentane). Found: C 28.68; H 7.13; B 64.32%. $C_4H_{12}B_{10}$. Calculated: C 28.55, H 7.19; B 64.26%.

9-Ethynyl-m-carborane (XIII). This compound was obtained in a similar way from (X). Yield, 0.8 g (87%), mp 120-121°C (pentane). Found: C 28.72; H 7.26; B 64.25%. $C_4H_{12}B_{10}$. Calculated: C 28.55; H 7.19; B 64.26%.

b) Synthesis from (XIV). A solution of 3.3 g (10 mmoles) of 9-(1',2'-dibromomethyl$_o$-o-carborane in 30 ml of absolute ether was added, with cooling (—30°C) and stirring, to $NaNH_2$, prepared from 1.2 g (0.5 g-at) Na in 120 ml of liquid ammonia, and the mixture was stirred for 1 h at —30°C. Then dry NH_4Cl was added, the ammonia was evaporated, and the residue was treated with water and extracted by ether. The extract was washed with water, and dried over $MgSO_4$. The ether was distilled in vacuo, and the residue was sublimed at 40°C (1 mm). Yield, 1.18 g (70%), mp 146-147°C (pentane). The compound was identified by comparing the melting point with that of a known sample, from IR and PMR spectra, and also by GLC.

9-Ethynyl-m-carborane (XIII). This compound was obtained in a similar way from (XV). Yield, 1.51 g (90%), mp 120-121°C (pentane).

CONCLUSIONS

The previously unknown 9-vinyl- and 9-ethynyl-o- and m-carboranes were obtained by the reaction of vinyl- and ethynylmagnesium halides with 9-iodo-o- and 9-iodo-m-carboranes, catalyzed by palladium complexes.

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