

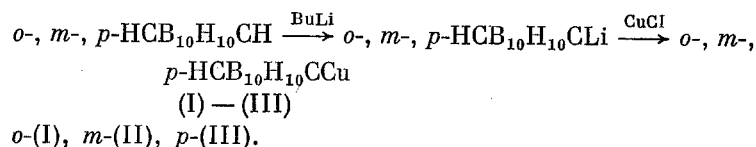
PREPARATION OF 1-ETHYNYL-*o*-, *m*-, AND *p*-CARBORANES FROM  
CARBORANYLCOPPER COMPOUNDS

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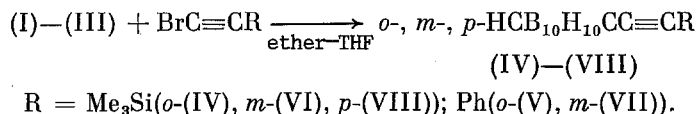
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Only two ethynylcarborane compounds containing an ethynyl group bound directly to a 1-carboranyl group are known; these are 1-ethynyl-*o*- and 1-ethynyl-2-phenyl-*o*-carborane, respectively [1-3], which were prepared via the reaction of decarborane with diacetylene and the appropriately substituted acetylene. 1-Ethynyl-*m*- and 1-ethynyl-*p*-carboranes are not known.

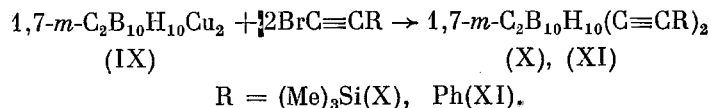
In the present paper we report the development of two convenient methods for the preparation of acetylenic derivatives of *o*-, *m*-, and *p*-carboranes from 1-*o*- (I), 1-*m*- (II), and 1-*p*-carboranylcopper (III) compounds, respectively; the latter compounds are themselves easily obtained from the corresponding 1-carboranyllithium compounds and CuCl in THF-ether solution:



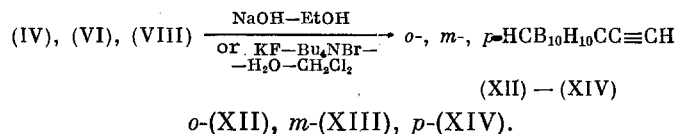
In the first method, 1-acetylenic *o*-, *m*-, and *p*-carborane derivatives are obtained via the reaction of compounds (I)-(III) with 1-bromo-2-trimethylsilyl- and 1-bromo-2-phenylacetylenes:



1,7-Diacetylene derivatives of *m*-carborane are prepared in an analogous manner from 1,7-carboranylenedicopper (IX):



The conversion of compounds (IV), (VI), and (VIII) into 1-ethynyl-*o*-(XII), *m*- (XIII), and *p*-carboranes (XIV) upon treatment with base and KF has also been studied. It was found that compounds (VI) and (VIII) were easily converted into (XIII) and (XIV) by basic hydrolysis in ethanol. The yield of (XII) prepared in this manner is low (20%), due to extensive resinification of (XII) (under the reaction conditions). When (IV) is treated instead with KF in ethanol at 20°C, the yield of (XII) is increased to 50%. A second, better method for the conversion of (IV) into (XII) was found; it involved reaction with KF in a two-phase system and resulted in an 80% yield of (XII):



Similarly, 1,7-diethynyl-*m*-carborane (XV) was prepared via basic hydrolysis of 1,7-bis(trimethylsilylethynyl)-*m*-carborane (X).

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TABLE 1. Yields, Physical Constants, and Elemental Analyses, as well as IR, Raman, and PMR Spectral Data for 1-(Trimethylsilylethynyl)-(IV), (V), (VI), (VIII); 1-(Phenylethynyl)-(V), (VII); 1-(trans- $\beta$ -Halovinyl)-o-, m-, and p-Carboranes (XXII) and 1,7-Di(trimethylsilylethynyl)-(X), 1,7-Di(phenylethynyl)-(XI), and 1,7-Di(trans- $\beta$ -Halovinyl)-m-Carboranes (XXIII) and (XXIV)

Compound	Yield, %	mp, °C (solvent) or bp, °C (p, mm Hg)	Molecular formula	Found/ Calculated, %				IR spectrum, $\nu$ , $\text{cm}^{-1}$	Raman spectrum, $\nu$ , $\text{cm}^{-1}$ , C $\equiv$ C bond	PMR spectrum, $\delta$ , ppm, $J_{\text{HH}}$ , Hz
				C	H	B	Si or halogen			
(IV)	66	122-123(3)	$\text{C}_7\text{H}_{20}\text{B}_{10}\text{Si}$	34.95 34.97	8.59 8.38	44.90 44.97	11.61 11.67	2195 w (C $\equiv$ C) 2600 v.s (BH) 3080 m (carb-H)	2187	0.19 s (9H, $(\text{CH}_3)_3\text{Si}$ ), 3.99 br.s (H, carb-H)
(V)	60	150-151(1)	$\text{C}_{10}\text{H}_{16}\text{B}_{10}$	49.25 49.16	6.54 6.60	44.42 44.24	-	-	-	-
(VI)	84	93-94(1)	$\text{C}_7\text{H}_{20}\text{B}_{10}\text{Si}$	35.08 34.97	8.29 8.38	44.92 44.97	11.65 11.67	2190 s (C $\equiv$ C) 2600 v.s (BH), 3070 m (carb-H)	-	0.15 s (9H, $(\text{CH}_3)_3\text{Si}$ ), 2.92 br.s (H, carb-H)
(VII)	81	62-63 methanol, 190-192(10)	$\text{C}_{10}\text{H}_{16}\text{B}_{10}$	49.33 49.16	6.66 6.60	44.03 44.24	-	2230 s (C $\equiv$ C) 2600 v.s (BH), 3060 m (C $\equiv$ C-H)	2225	-
(VIII)	86	75-76(1)	$\text{C}_7\text{H}_{20}\text{B}_{10}\text{Si}$	34.84 34.97	8.31 8.38	45.23 44.97	11.42 11.67	-	-	-
(X)	35	76-77 methanol 125-126(1)	$\text{C}_{12}\text{H}_{28}\text{B}_{10}\text{Si}_2$	42.84 42.81	8.44 8.38	32.10 32.11	16.68 16.69	2190 s (C $\equiv$ C) 2600 v.s (BH)	-	-
(XI)	32	140-141 acetone	$\text{C}_{18}\text{H}_{20}\text{B}_{10}$	62.72 62.76	5.83 5.85	31.32 31.38	-	2235 m (C $\equiv$ C) 2600 v.s (BH)	2234	-
(XVIII)	53	115-117 ethanol	$\text{C}_4\text{H}_{13}\text{B}_{10}\text{Cl}$	23.73 23.47	6.67 6.40	-	17.38 17.32	930 s (p-CH), 1300 m. ( $\delta$ -CH), 1625 s (C $\equiv$ C), 2600 v.s (BH), 3070 s (C $\equiv$ C-H)	-	3.46 br.s (H, C $\equiv$ C-H), 5.94 d and 6.46 d (2H, CH $\equiv$ CH, $J_{\text{HH}}$ = 13.5)
(XIX)	50	135-137 ethanol	$\text{C}_4\text{H}_{13}\text{B}_{10}\text{I}$	16.34 16.22	4.46 4.42	36.54 36.51	43.19 42.85	935 s (p-CH), 1305 w. ( $\delta$ -CH), 1605 m (C $\equiv$ C), 2600 v.s (BH), 3070 s (carb-H)	-	3.57 br.s (H, carb-H), 6.56 d and 6.99 d (2H, CH $\equiv$ CH, $J_{\text{HH}}$ = 14.2)
(XX)	60	82-83 ethanol	$\text{C}_4\text{H}_{13}\text{B}_{10}\text{Cl}$	23.65 23.47	6.89 6.40	-	-	930 s (p-CH), 1300 m. ( $\delta$ -CH), 1625 s (C $\equiv$ C), 2600 v.s (BH), 3070 s (carb-H)	-	3.00 br.s (H, C $\equiv$ C-H), 5.97 d and 6.38 d (2H, CH $\equiv$ CH, $J_{\text{HH}}$ = 13.3)
(XXI)	55	119-121 ethanol	$\text{C}_4\text{H}_{13}\text{B}_{10}\text{I}$	16.41 16.22	4.47 4.42	36.71 36.51	42.40 42.85	940 s (p-CH), 1305 w. ( $\delta$ -CH), 1605 m (C $\equiv$ C), 2600 v.s (BH), 3070 s (carb-H)	-	2.87 br.s (H, C $\equiv$ C-H), 6.29 d and 6.50 d (2H, CH $\equiv$ CH, $J_{\text{HH}}$ = 14.3)
(XXII)	54	147-149 ethanol	$\text{C}_4\text{H}_{13}\text{B}_{10}\text{I}$	16.44 16.22	4.57 4.42	36.67 36.51	42.35 42.85	940 s (p-CH), 1305 w. ( $\delta$ -CH), 1605 m. (C $\equiv$ C), 2600 v.s (BH), 3070 s (carb-H)	-	2.60 br.s (H, carb-H), 5.99 d and 6.49 d (2H, CH $\equiv$ CH, $J_{\text{HH}}$ = 14.0)
(XXIII)	54	106-108 ethanol	$\text{C}_6\text{H}_{14}\text{B}_{10}\text{Cl}_2$	26.59 27.16	5.25 5.32	40.65 40.78	26.57 26.74	930 s (p-CH) 1300 m ( $\delta$ -CH) 1625 m (C $\equiv$ C), 2600 v.s (BH), 3070 s (carb-H)	-	5.95 d and 6.39 d (2H, CH $\equiv$ CH, $J_{\text{HH}}$ = 13.3)
(XXIV)	42	98-100 ethanol	$\text{C}_3\text{H}_{14}\text{B}_{10}\text{I}_2$	16.45 16.07	3.29 3.15	-	-	940 s (p-CH), 1305 w. ( $\delta$ -CH) 1605 m (C $\equiv$ C), 2600 vs (BH), 3070 s (carb-H)	-	6.28 d and 6.50 d (2H, CH $\equiv$ CH, $J_{\text{HH}}$ = 14.3)

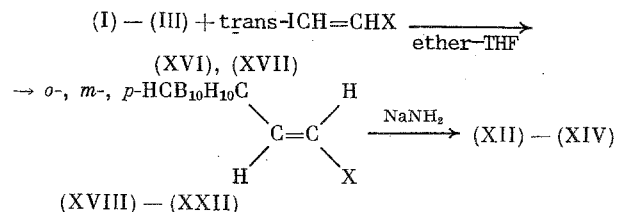
\*PMR spectra were obtained on 20% solutions in  $\text{CCl}_4$  relative to HMDS; chemical shifts are reported relative to TMS. C $\equiv$ C on the carborane nucleus.

TABLE 2. Yields, Physical Constants, and Elemental Analyses, as well as IR, Raman, and PMR Spectra of 1-Ethynyl-o-, m-, and p-Carboranes (XII)-(XIV) and 1,7-Diethynyl-m-carborane (XV)

Compound	Yield, %		mp, °C (sublimation), bp, °C (p, mm Hg)	Molecular formula	Found/ Calculated, %			IR spectrum, $\nu$ , $\text{cm}^{-1}$	Raman spectrum, $\nu$ , $\text{cm}^{-1}$ , C $\equiv$ C bond	PMR spectrum, $\delta$ , ppm
	by method I	by method 2 and halogens in (XVIII)- (XXIV)			C	H	B			
(XII)	80	60 (Cl) 53 (I)	98-99 (sublimation)	$\text{C}_4\text{H}_{12}\text{B}_{10}$	$\frac{28.43}{28.55}$	$\frac{7.27}{7.49}$	$\frac{64.42}{64.25}$	2140 w. (C $\equiv$ C), 2600 vs (BH), 3070 m (Ccarb-H), 3295 s (=CH)	2136	2.20 s (H, =CH) 3.86 brs (H, carb- H)
(XIII)	92	87 (Cl) 80 (I)	92-93 (sublimation)	$\text{C}_4\text{H}_{12}\text{B}_{10}$	$\frac{28.52}{28.55}$	$\frac{7.22}{7.49}$	$\frac{64.06}{64.25}$	2600 vs. (BH) 3065 m. (Ccarb-H) 3310 s (=CH)	2140	2.01 s (H, =CH), 2.95 brs (H, carb-H)
(XIV)	90	62 (I)	88-89 (sublimation)	$\text{C}_4\text{H}_{12}\text{B}_{10}$	$\frac{28.40}{28.55}$	$\frac{7.23}{7.19}$	$\frac{64.34}{64.25}$	2600 vs. (BH), 3065 m (carb-H), 3315 s (=CH)	2142	2.01 s (H, =CH), 2.65 brs (H, carb-H)
(XV)	85	75 (Cl) 70 (I)	81-82(5)	$\text{C}_6\text{H}_{12}\text{B}_{10}$	$\frac{37.32}{37.48}$	$\frac{6.36}{6.29}$	$\frac{56.07}{56.23}$	2140 w. (C $\equiv$ C), 2600 vs. (BH), 3320 s (=CH)	-	-

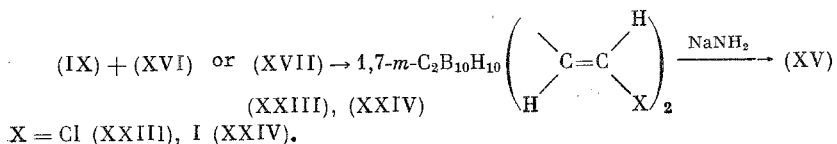
\*PMR spectral acquisition parameters were the same as reported in Table 1.

The second alternative method for the preparation of 1-ethynylcarboranes (XII)-(XIV) involved reaction of compounds (I)-(III) with trans-1,2-diiodo-(XVI) or trans-1-chloro-2-iodoethylene (XVII), followed by dehydrohalogenation of the resulting 1-(trans-β-halovinyl)-o-, m-, and p-carboranes (XVIII)-(XXII) with NaNH<sub>2</sub> in liquid NH<sub>3</sub>:



X = Cl(XVI), I(XVII); X = Cl(o-(XVIII), m-(XX)); X = I(o-(XIX), m-(XXI), p-(XXII))

In an analogous manner, reaction of 1,7-m-carboranylenedicopper (IX) with compounds (XVI) and (XVII) gave 1,7-di-(trans-β-halovinyl)-m-carboranes (XXIII) and (XXIV), which were in turn converted into 1,7-m-diethynylcarborane (XV):



It should be noted that in the reactions of 1-carboranylcopper [compounds (I)-(III)] and 1,7-dicarboranylenedicopper (IX) compounds with dihaloethylene derivatives (XVI) and (XVII), only the I group is replaced with a carboranyl group, and the reactions occur with retention of configuration; the 1-(β-halovinyl)carboranes (XVIII)-(XXII) and 1,7-di(β-halovinyl)-m-carboranes (XXIII) and (XXIV) all exhibit the trans configuration. This is supported unequivocally by their IR and PMR spectra [compounds (XVIII)-(XXIV)], and by the differences between their physical constants and analogous data for 1-(cis-β-halovinyl)carboranes [4].

Dehydrohalogenation of compounds (XVIII)-(XXII) requires 3 equiv. of NaNH<sub>2</sub>, since 2 moles of NaNH<sub>2</sub> are consumed via metallation of the C<sub>carb</sub>-H and ≡C-H bonds; by analogy, dehydrohalogenation of compounds (XXIII) and (XXIV) requires 4 equiv. of NaNH<sub>2</sub>.

Both methods for the preparation of ethynyl- and diethynylcarboranes (XII)-(XV) are characterized by facile reactions which proceed in high yield.

1-Vinyl-o- (XXV) and 1-vinyl-m-carborane (XXVI) could be prepared in an analogous manner by reaction of the carboranylcopper compounds (I) and (II) with CH<sub>2</sub>=CHI, in 40 and 70% yields respectively.

The 1-vinylcarboranes (XXV) and (XXVI) were difficult to separate from the starting carboranes; complete separation of (XXVI) required workup of the reaction mixture with bromine. This resulted in the conversion of (XXVI) into 1-(1'-2'-dibromoethyl)-m-carborane (XXVII), from which the carborane precursor was easily isolated by vacuum sublimation; subsequent treatment with Zn powder resulted in the conversion of (XXVII) into (XXVI).

1-Vinyl-o-carborane (XXV) has been prepared previously by the reaction of decaborane with vinylacetylene [5, 6]; compound (XXVI) has been synthesized by us for the first time, and the method described herein can be heartily recommended.

The yields, physical constant, elemental analyses, as well as IR, Raman, and PMR spectral data for the compounds described herein are presented in Tables 1 and 2.

#### EXPERIMENTAL

trans-1,2-Diiodoethylene [7], trans-1-chloro-2-iodoethylene [8], Me<sub>3</sub>SiC≡CR [9], and PhC≡CBr [10] were prepared according to known methods. GLC analyses were carried out in an LKhM-8MD chromatograph using a 2 m × 3 mm column with 10% SKTFT-50x as the mobile phase on silanated Chromatone N-AW-DMCS (particle size 0.200-0.250 mm); a katharometer detector was used, at a column temperature of 120-250°C and a helium flow rate of 50 ml/min. IR spectra were recorded on a UR-20 spectrophotometer; solid samples were examined as KBr pellets, liquid samples as thin films. Raman spectra were obtained on a Raman or HG-2S spectrometer equipped

with an Ar<sup>+</sup> laser at a 5145 Å excitation energy. PMR spectra were recorded on an RYa-2309 spectrometer at an operating frequency of 90 MHz.

1-o-, m-, and p-Carboranylcopper (I)-(III). A solution of 2.88 g (0.02 mole) of o-, m-, or p-carborane in 30 ml absolute ether was cooled to 0-5°C under a N<sub>2</sub> atmosphere and 0.02 mole of BuLi in hexane (17 ml, 1.18 M) was added with stirring. The cooling bath was removed, and after 15 min the mixture was refluxed for 5 min, then cooled again to -10 to -20°C while 2.47 g (0.025 mole) of anhydrous CuCl in 50 ml of dry THF (cooled to 0°C) was added in small portions under a N<sub>2</sub> atmosphere. The cooling bath was removed, and the mixture was stirred for 2 h, then heated at 40°C for 10 min. The resulting suspension of carboranylcopper was dark orange in color and was used in subsequent reactions without purification.

1,2-o- and 1,7-m-Carboranylenedicopper (IX). These were prepared in an analogous manner from 2.88 g (0.02 mole) o- or m-carborane in 50 ml absolute ether, 0.04 mole BuLi in hexane (34 ml, 1.18 M), and 4.94 g (0.05 mole) anhydrous CuCl in 50 ml dry THF.

1-Trimethylsilylethynyl- and 1-(Phenylethynyl)-o-, m-, and p-carboranes (IV)-(VIII). A suspension of 1-o-, m-, or p-carboranylcopper, prepared as described above from 5.77 g (0.04 mole) o-, m-, or p-carborane in 60 ml absolute ether, 0.04 mole BuLi in hexane (37.4 ml, 1.07 M), and 5.0 g (0.05 mole) anhydrous CuCl in 100 ml dry THF, was treated at 20°C under a N<sub>2</sub> atmosphere with 8.86 g (0.05 mole) of 1-bromo-2-trimethylsilylacetylene or 9.05 g (0.05 mole) of 1-bromo-2-phenylacetylene with stirring. The mixture was stirred for 1 h at 20°C, refluxed for 2 h, then cooled to 0°C and treated with 5% aqueous HCl with stirring. The mixture was extracted with ether, and the ether extract was washed with 5% HCl, water to pH 7, and finally dried over Na<sub>2</sub>SO<sub>4</sub> or MgSO<sub>4</sub>. The ether was evaporated, and compounds (IV)-(VIII) were either isolated from the residues by column chromatography on silica gel with hexane or else by distillation under vacuum to give first any unreacted carborane, followed by the acetylenic derivative.

1,7-Bis(trimethylsilylethynyl)- and 1,7-Bis(phenylethynyl)-m-carborane (X) and (XI). These were obtained in an analogous manner from 5.77 g (0.05 mole) m-carborane in 100 ml absolute ether, 0.08 mole BuLi in hexane (74.8 ml, 1.07 M), 10 g (0.1 mole) anhydrous CuCl in 100 ml dry THF, and either 17.72 g (0.1 mole) 1-bromo-2-trimethylsilylacetylene or 18.1 g (0.1 mole) 1-bromo-2-phenylacetylene. The compounds were isolated and purified by fractional distillation under vacuum and subsequent recrystallization.

1-(trans-β-Halovinyl)-o-, m-, and p-carborane (XVIII)-(XXII). A solution of 5.6 g (0.02 mole) trans-1,2-diiodoethylene or 3.77 g (0.02 mole) trans-1-chloro-2-iodoethylene in 50 ml dry THF under a N<sub>2</sub> atmosphere was treated with stirring at 20°C with 1-o-, m-, or p-carboranylcopper, prepared from 2.88 g (0.02 mole) o-, m-, or p-carborane in 30 ml absolute ether, 0.02 mole BuLi in hexane (17 ml, 1.18 M), and 2.47 g (0.025 mole) anhydrous CuCl in 50 ml dry THF. The mixture was refluxed with stirring for 2 h under N<sub>2</sub>, cooled, and decomposed with 15% HCl, followed by dilution with water and extraction with ether. The extract was washed with dilute HCl and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the solid residue was fractionally distilled under vacuum. Carborane and dihaloethylene were separated at 30-60°C (1 mm), followed by distillation of the 1-(β-halovinyl)carborane at 100-140°C (1 mm), which was then recrystallized from ethanol.

1,7-Bis(trans-β-halovinyl)-m-carborane (XXIII) and (XXIV). These were prepared similarly from 2.88 g (0.02 mole) m-carborane in 50 ml absolute ether, 0.04 mole BuLi in hexane (34 ml, 1.18 M), 4.94 g (0.05 mole) anhydrous CuCl in 50 ml dry THF, and a solution of either 11.2 g (0.04 mole) trans-1,2-diiodoethylene or 7.6 g (0.04 mole) trans-1-chloro-2-iodoethylene in 50 ml absolute THF. Fractional distillation under vacuum gave m-carborane and dihaloethylene between 30-60°C (1 mm), followed by 1,7-bis(trans-β-halovinyl)-m-carborane at 100-140°C (1 mm), which was then recrystallized from ethanol.

1-Ethynyl-o-carborane (XII). A mixture of 2.4 g (0.1 mole) 1-trimethylsilylethynyl-o-carborane, 5.8 g (0.1 mole) KF, 0.1 g Bu<sub>4</sub>NBr, 10 ml water and 25 ml CH<sub>2</sub>Cl<sub>2</sub> was stirred vigorously at 20°C for 10-15 min until all of the starting material had disappeared (according to TLC on Silufol with hexane). The lower layer was separated, the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the combined extracts were washed with water and dried over MgSO<sub>4</sub>. Solvent was removed under vacuum, and (XII) was isolated by distillation at 50-130°C (1 mm).

1-Ethynyl-m- and p-carborane (XIII) and (XIV). Method 1. A solution of 2.4 g (0.1 mole) 1-(trimethylsilylethynyl)-o-, m-, or p-carborane in 25 ml ethanol was diluted with an equal

volume of 1% NaOH solution in ethanol and maintained at 20°C for 10-15 min. After disappearance of the starting trimethylsilylethynylcarborane was observed (by TLC on Silufol with hexane), the excess base was neutralized with dilute HCl, diluted further with 3-4 quantities of water, and the resulting precipitate of ethynylcarborane was extracted into ether, washed with water, and dried over  $\text{MgCO}_4$ . The ether was evaporated and the ethynylcarborane was distilled at 30-100°C (1 mm).

Method 2.  $\text{NaNH}_2$ , prepared from 0.7 g (0.03 g-atom) Na in 150 ml liquid  $\text{NH}_3$  in the presence of a catalytic amount of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , was treated with stirring at -30 to -40°C with a solution of 2.96 g (0.01 mole) 1-(trans- $\beta$ -iodovinyl)carborane or 2.05 g (0.01 mole) 1-(trans- $\beta$ -chlorovinyl)carborane in 30 ml of absolute ether. After 30 min dry  $\text{NH}_4\text{Cl}$  (5.3 g, 0.1 mole) was added to the mixture in small portions. The ammonia was evaporated and the residue was worked up with water and extracted with ether. The extracts were washed with water and dried over  $\text{Na}_2\text{SO}_4$ . Ether was evaporated and the ethynylcarborane was distilled at 50-80°C (1 mm).

1,7-Diethynyl-m-carborane (XV). Method 1. This was obtained from 6.73 g (0.02 mole) 1,7-bis(trimethylsilylethynyl)-m-carborane in 50 ml ethanol and an equal volume 1% NaOH solution in ethanol.

Method 2.  $\text{NaNH}_2$ , prepared from 0.64 g (0.028 g-atom) Na in 150 ml liquid ammonia in the presence of catalytic  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , and 3.14 g (0.007 mole) 1,7-bis(trans- $\beta$ -iodovinyl)-m-carborane or 1.86 g (0.007 mole) 1,7-bis(trans- $\beta$ -chlorovinyl)-m-carborane and 3.74 g (0.07 mole) dry  $\text{NH}_4\text{Cl}$ , gave (XV).

1-Vinyl-o- and m-carborane (XXV) and (XXVI), and 1-(1',2'-Dibromoethyl)-m-carborane (XXVII). A suspension of 1-o- or 1-m-carboranyl copper, prepared from 5.76 g (0.04 mole) o- or m-carborane in 60 ml absolute ether, 0.04 mole BuLi (35.7 ml, 1.12 M) in hexane, and 5.0 g (0.05 mole) anhydrous CuCl in 100 ml dry THF, was treated with 8 g (0.052 mole)  $\text{CH}_2=\text{CHI}$  and refluxed 6 h. According to GLC analysis, the reaction products consisted of 40% vinyl-o-carborane or 75% vinyl-m-carborane, respectively. The mixture was decomposed with 18% HCl, extracted with ether, washed with water, dried over  $\text{MgSO}_4$ , and finally concentrated to remove ether. The residue (6.8 g) was dissolved in 50 ml  $\text{CCl}_4$  and treated with a solution of 4.8 g (0.03 mole) bromine in 10 ml  $\text{CCl}_4$ , and then refluxed for 16 h. According to GLC, the mixture contained 25% unreacted vinyl-m-carborane at this point. Further reflux under UV irradiation resulted in the reaction going to completion within 4 h. The mixture was worked up with  $\text{Na}_2\text{SO}_3$  solution, washed with water, and dried over  $\text{MgSO}_4$ . The m-carborane impurity remaining was distilled under vacuum, and the residue was sublimed. Yield, 7 g (71%) of 1-(1'-2'-dibromoethyl)-m-carborane, bp 116-118°C (1 mm). Found: C 14.80; H 4.25; Br 48.18%.  $\text{C}_4\text{H}_{14}\text{B}_{10}\text{Br}_2$ . Calculated: C 14.56; H 4.28; Br 48.42%.

A solution of 1 g (3 mmole) of 1-(1',2'-dibromoethyl)-m-carborane in 40 ml ethanol was treated with 2 g of Zn dust and refluxed 4 h. Yield, 0.36 g (70%) of 1-vinyl-m-carborane, mp 48-49°C.

## CONCLUSIONS

Two methods have been developed for the preparation of 1-ethynyl-o-, m-, and p-carboranes: reaction of 1-o-, m-, and p-carboranyl copper derivatives with 1-bromo-2-trimethylsilylacetylene and subsequent decomposition of the C-Si bond in the trimethylsilylethynylcarboranes with either ethanolic base or KF in a two-phase system, and, secondly, reaction of 1-o-, m-, and p-carboranyl copper with trans-1-halo-2-iodoethylenes (halogen = Cl or I), followed by dehydrohalogenation of the resulting 1-(trans- $\beta$ -halovinyl)carboranes with sodium amide in liquid ammonia.

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