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PREPARATION AND STUDY OF DECACHLORO-*o*-CARBORANE (o-$B_{10}Cl_{10}C_2H_2$)

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SUMMARY

The final product of photochemical chlorination of *o*-carborane was established as decachloro-*o*-carborane (o-$B_{10}Cl_{10}C_2H_2$) and not the "undecachlorocarborane" according to Schroeder, Heying and Reiner. Undecachloro-*o*-carborane prepared by these authors was identical with decachloro-*o*-carborane. In aqueous ethanol, decachloro-*o*-carborane titrates as a monoprotic acid and has a pK_a value of 6.89 (50% ethanol). Decachloro-*o*-carborane gives stable adducts with $(C_2H_5)_3N$, $(CH_3)_3N$, $(CH_3)_2SO_4$ and $(CH_3)_2NCHO$. The reaction of chlorine with the mono-triethylammonium salt of decachloro-*o*-carborane produced dodecachloro-*o*-carborane. The same reaction with bromine gave 1,2-dibromodecachloro-*o*-carborane.

INTRODUCTION

The photochemical chlorination of *o*-carborane (o-$B_{10}H_{10}C_2H_2$) has been described by Schroeder, Heying and Reiner[1], and by Zakharkin, Stanko and Klimova[2,3]. Both papers report the same results, except those concerning the final chlorination product of *o*-carborane. In the Russian paper, this reaction involves B–H bonds without any participation of C–H bonds but the American chemists report that decachloro-*o*-carborane is not the final product, and that the reaction proceeds further to undecachloro-*o*-carborane (o-$B_{10}Cl_{10}C_2HCl$). Moreover, the decachloro-*o*-carboranes, prepared by the two groups of investigators, differ somewhat in melting points, and in IR-spectra in the range 700–1000 cm^{-1}. In a subsequent communication, Schroeder *et al.* studied some reactions of undecachloro-*o*-carborane[4]. Photochemical chlorination of *m*-carborane (m-$B_{10}H_{10}C_2H_2$) produced decachloro-*m*-carborane, involving no C–H bonds[3,5]. Smith, Knowles and Schroeder reported that photochlorination of dibromo-*o*-carborane and dibromo-*m*-carborane led to dibromooctachloro-*o*-carborane and *B*-dibromooctachloro-*m*-carborane without C–H participation. To resolve the differences reported[1-3], we have carried out a more detailed investigation of the exhaustive photochlorination of *o*-carborane. We were unable to reproduce the data of ref. 1. Decachloro-*o*-carborane was always the final product which would not further chlorinate under the conditions described[1]. Our pure decachloro-*o*-carborane had m.p. 274.5–275°.

In the present work we found that the "undecachlorocarborane" of Schroeder, Heying and Reiner, was actually decachlorocarborane identical with our *o*-isomer, a final product in the photochlorination of carborane. "Undecachlorocarborane" of ref. 1 has m.p. 279° and the m.p. of decachloro-*o*-carborane was 259°. The following comparison shows that our decachloro-*o*-carborane and "undecachlorocarborane" are identical.

The two compounds have identical IR spectra (Fig. 1). A characteristic feature of these spectra is the fact that besides a complete absence of the B–H bond absorbance at 2600 cm^{-1}, the absorbance band near 800 cm^{-1}, found in the spectra of Schroeder's octachloro-*o*-carborane and "decachloro-*o*-carborane" (*cf.* ref. 1), was absent here. It should be noted that 9,12-dibromooctachloro-*o*-carborane also has no such band.

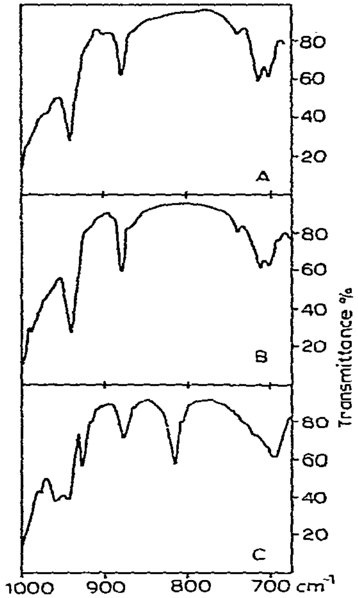
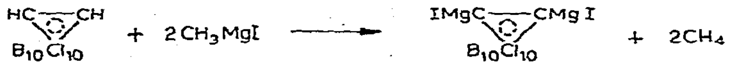


Fig. 1. IR spectra: (A), our decachloro-*o*-carborane; (B), "undecachloro-*o*-carborane"[1]; (C), decachloro-*o*-carborane of Schroeder *et al.*[1].

The two compounds have practically equivalent chemical shifts in the PMR spectra: 4.06 τ for decachloro-*o*-carborane (reference compound, hexamethyldisiloxane) and 3.96 τ for "undecachlorocarborane" (referenced to tetramethylsilane). The chemical shift for "decachloro-*o*-carborane" is 5.70 τ. We also give here, for a comparison, the shifts for 9,12-dibromooctachloro-*o*-carborane (3.93 τ), methyldecachloro-*o*-carborane (4.17 τ) and decachloro-*m*-carborane (4.85 τ) (referenced to hexamethyldisiloxane).

"Undecachlorocarborane" titrates as a monoprotonic acid in aqueous ethanol[1]. We have shown that decachloro-*o*-carborane and 9,12-dibromooctachloro-*o*-carborane also titrate as monoprotic acids in the same solvent. However, in the determination of active hydrogen by the method of Tzerevitinov, two moles of methane are evolved in the reaction with CH_3MgI in dibutyl ether:



In analogy with decachloro-*o*-carborane, decachloro-*m*-carborane in aqueous ethanol titrates as a monoprotic acid. However, in the reaction with CH_3MgI, two moles of methane were evolved.

We have measured the pK_a-values for decachloro-*o*-carborane, 9,12-dibromooctachloro-*o*-carborane, methyldecachloro-*o*-carborane and decachloro-*m*-carborane in 50% ethanol and compared these values with those of some acids (Table 1).

TABLE 1

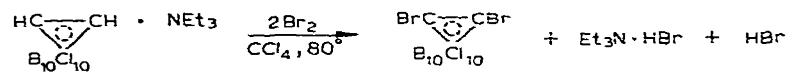
pK_a VALUES IN 50% ETHANOL

No.	Compound	pK_a	No.	Compound	pK_a	Reference
1	*o*-$B_{10}Cl_{10}C_2H_2$	6.89	5	*p*-NH_2-*o*-CH_3-C_6H_3COOH	6.83	7
2	*o*-$B_{10}Br_2Cl_8C_2H_2$	6.95	6	*p*-NO_2-C_6H_4-OH	7.68	8
			7	C_6H_5SH	7.78	8
3	*o*-$B_{10}Cl_{10}C_2H(CH_3)$	6.90	8	*p*-Cl-C_6H_4SH	7.06	8
4	*m*-$B_{10}Cl_{10}C_2H_2$	9.19	9	$CH_3(CH{=}CH)_2COOH$	7.00	9

The data of this table show that decachloro-*o*-carborane and some other decahalo-*o*-carboranes containing the C–H bond are strong C-acids comparable in strength to carboxylic acids.

Decachloro-*o*-carborane and triethylamine gave only the monotriethylammonium salt identical in melting point with the monotriethylammonium salt of the "undecachloro-*o*-carborane" of Schroeder *et al.* Trimethylamine and decachloro-*o*-carborane gave the monotrimethylammonium salt. The corresponding trialkylammonium salts were obtained from methyl- and ethyldecachloro-*o*-carboranes. All these salts are listed in Table 2.

Decachloro-*o*-carborane of Schroeder *et al.*[1] titrates as a diprotic acid in aqueous ethanol and gives the bis(triethylammonium) salt in the reaction with triethylamine. The reaction of chlorine with the monotriethylammonium salt of "undecachloro-*o*-carborane" in boiling CCl_4 gives dodecachloro-*o*-carborane[4]. We have found that in the case of the monotriethylammonium salt of decachloro-*o*-carborane, the same reaction proceeded with evolution of hydrogen chloride and formation of dodecachlorocarborane. The reaction with bromine under the same conditions produced 1,2-dibromodecachloro-*o*-carborane with consumption of two moles of bromine.



The first mole of bromine is easily consumed at room temperature.

Dodecachloro-*o*-carborane is probably formed owing to the reaction of chlorine with the salt giving triethylamine hydrochloride and undecachloro-*o*-carborane which, being essentially a strong acid, attracts hydrogen chloride from triethylamine hydrochloride to give the salt. The latter may be further chlorinated into dodecachloro-*o*-carborane.

An analogous procedure should be observed in the bromination to 1,2-dibromodecachloro-*o*-carborane.

TABLE 2

TRIALKYLAMMONIUM SALTS OF DECACHLORO-*o*-CARBORANES

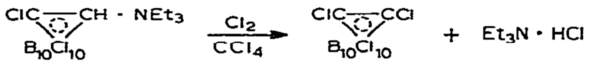
No.	Compound	M.p. (°C)	Yield (%)	Mol. wt.	C		H		B		Cl		N	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1	$B_{10}Cl_{10}C_2H_2NEt_3$	165–166	100	590.0	16.29	16.21	2.90	2.99	18.34	18.41	60.10	60.19	2.37	2.29
2	$B_{10}Cl_{10}C_2HMeNEt_3$	120–140 (dec.)	83	604.0	17.90	18.25	3.17	3.23	17.91	17.87	58.70	59.06	2.32	2.61
3	$B_{10}Cl_{10}C_2HEtNEt_3$	146 (dec.)	81	618.1	19.43	19.35	3.42	3.46	17.51	17.71	57.37	57.82	2.27	2.66
4	$B_{10}Cl_{10}C_2H_2NMe_3$	150–160 (dec.)	91	547.9	10.96	11.19	2.02	2.12	19.75	20.01	64.71	63.80 66.01	2.56	2.60
5	$B_{10}Cl_{10}C_2HMeNMe_3$	170–190 (dec.)	95	561.9	12.82	12.76	2.33	2.18	19.25	19.00	63.10	63.59	2.49	2.52

TABLE 3

THE ADDUCTS OF DECAHALO-*o*-CARBORANES WITH Me_2SO AND Me_2NCHO

No.	Compound	M.p. (°C)	Yield[c]	Mol.wt.	C		H		B		Hal.		S		N	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1	$B_{10}Cl_{10}C_2H_2Me_2SO$	159–160[a] dec.	94[a]89[b]90[c]	566.9	8.47	8.45	1.42	1.39	19.08	19.32	62.54	62.23	5.66	5.18		
2	$B_{10}Cl_{10}C_2HMeMe_2SO$	150–151[a] dec.	90[b]	581.0	10.34	10.45	1.74	1.84	18.62	18.39	61.03	61.25	5.52	5.52		
3	$B_{10}Cl_{10}C_2HEtMe_2SO$	158[b] dec.	77[b]	595.0	12.11	11.94	2.03	2.03	18.18	17.93	59.59	59.66	5.39	5.64		
4	$B_{10}Br_2Cl_8C_2H_2Me_2SO$	176[a] dec.	61[c]	655.9	7.33	7.74	1.23	1.32	16.50	16.31	43.25		4.89			
5	$B_{10}Cl_{10}C_2H_2Me_2NCHO$	151.5–153.5[a] dec.	89[a]92[b]	561.9	10.69	11.03	1.61	1.49	19.26	19.23	63.10	62.79			2.49	2.49
6	$B_{10}Cl_{10}C_2HMeMe_2NCHO$	145–151[a]	87[a]90[b]72[c]	575.9	12.51	12.62	1.93	1.98	18.79	18.66	61.56	61.27			2.43	2.52

[a] Recrystallized from hexane–ether mixture. [b] Recrystallized from hexane. [c] The yield is indicated in %(theory). The upper right indice corresponds to a synthetic method (*cf.* Experimental).



It has been shown experimentally, that decachloro- and other decahalo-*o*-carboranes containing C–H bonds, give adducts not only with strong bases (triethylamine and trimethylamine) but unusual and stable 1 : 1 adducts with such Lewis' bases as dimethylsulfoxide and dimethylformamide. These adducts are shown in Table 3. The nature of the adducts will be discussed in detail in the next communication.

The data on the integral intensities[10] of the C–H bonds in the IR spectra of decachloro-, 9,12-dibromooctachloro-, methyl- and ethyl-decachloro-*o*-carboranes and decachloro-*m*-carboranes convincingly support the existence of two C–H bonds in our decachloro-*o*-carborane (Table 4).

TABLE 4

INTEGRAL INTENSITIES OF THE C–H BONDS

No.	Compound	$\times l\cdot 10^3\cdot mole^{-1}\cdot cm^{-2}$	No.	Compound	$\times l\cdot 10^3\cdot mole^{-1}\cdot cm^{-2}$
1	o-$B_{10}Cl_{10}C_2H_2$	13.84[a]	4.	o-$B_{10}Cl_{10}C_2H$-(C_2H_5)	10.66
2	o-$B_{10}Br_2Cl_8C_2H_2$	13.13[a]	5.	m-$B_{10}C_{10}C_2H_2$	11.68[a]
3	o-$B_{10}Cl_{10}C_2H(CH_3)$	10.98			

[a] Per one C–H bond.

The above data individually identify our decachloro-*o*-carborane with the "undecachlorocarborane" of Schroeder, Heying and Reiner and indicate that the final product in photochlorination should be decachloro-*o*-carborane.

EXPERIMENTAL

The solvents and reagents used were dried and purified by standard procedures.

The PMR-spectra were taken in acetonitrile solution using a Hitachi H-60 apparatus with hexamethylsiloxane as a reference standard. Chemical shifts were recorded in the τ-scale.

The IR spectra were taken in the range 400–3700 cm^{-1} using a UR-10 double-beam spectrophotometer. The samples were pelleted with potassium bromide.

The melting points are uncorrected and were determined in sealed capillaries.

Decachloro-o-carborane

4 g (0.0278 mole) of *o*-carborane was dissolved in 400 ml of CCl_4. The mixture

was refluxed and irradiated with the UV light (PRK-4 lamp) and chlorine was passed through. After 7–10 min a large amount of solid precipitated; this disappeared after another 10–15 min, and the decolourisation of chlorine proceeded more slowly. After 1.5–3 h, the hot mixture was filtered and the filtrate cooled to 5°. 10–12 g (73–88% theory) of decachloro-*o*-carborane was obtained, m.p. 274.5–276 (CCl_4). (Found: C, 4.87; H, 0.60; B, 22.01; Cl, 72.65. $B_{10}Cl_{10}C_2H_2$ calcd.: mol. wt., 488.8; C, 4.91; H, 0.41; B, 22.14; Cl, 72.54%.) The chlorination period may vary depending on the intensity of UV light and the purity of the carborane and CCl_4. The completion of reaction may be controlled either by means of IR-spectroscopy withdrawing samples and recording the IR-spectra near 2600 cm^{-1}, the absorption band of the B–H bond, or by the melting point of the final product.

Decachloro-m-carborane was prepared by:

(*a*) *chlorination of m-carborane* using an analogous procedure to that for decachloro-*o*-carborane. The chlorination period was 6 h and gave 95% yield, m.p. 232–233° (CCl_4).

(*b*) *isomerization of decachloro-o-carborane.* 4 g (0.0082 mole) of decachloro-*o*-carborane was heated in an argon atmosphere in a metallic ampoule at 350° for 7 h. The product was dissolved in ether and the solution washed with water, 5% HCl and water until a neutral reaction was obtained. The ethereal solution was separated, dried over calcined $MgSO_4$ and evaporated. Decachloro-*m*-carborane was sublimed *in vacuo* (150°, 3 mm Hg) and recrystallized from CCl_4. The yield was 2.44 g (61% theory). m.p. 232–233°.

Dibromooctachloro-o-carborane was obtained by the method already described[6].

Volumetric titration of halocarboranes (*cf. Table* 5)

The weighed sample (0.002 mole) was dissolved in alcohol and titrated with a 0.1 *N* solution of KOH (phenolphthalein as indicator). Decachlorocarborane and dibromooctachlorocarborane titrate as monoprotonic acids in aqueous ethanol. The titration of octachlorocarborane requires less alkali than that for even one CH-group, and the results were not reproducible.

Dissociation constants of halocarboranes

These were calculated using the formula, $pK_a = pH + \log[HA] - \log[A^-]$. A 0.01 *N* solution of KOH and 0.01 *M* solutions of halocarboranes in 50% (wt.) alcohol were prepared. The pH-values at various degrees of neutralization were measured by a "Radiometer", type PHM-4c pH-meter at 20° (no special temperature control was used). The results are shown in Table 6.

Decachloro-, dibromooctachloro- and *C*-methyldecachloro-*o*-carboranes are stable at pH < 8. After 3 days the pH-values for two samples of decachloro-*o*-carborane (equal to 6.40 and 7.20) decreased by 0.23 and 0.20, respectively. At pH > 8 a considerable decrease in this value with time was observed indicating that decachloro-*o*-carborane was decomposing.

Decachloro-*m*-carborane was also unstable under the above conditions; 1.5 h after mixing 6.99 ml of a 0.01 *N* KOH solution ($k = 0.9681$) with 13.1 ml of a 0.01 *M* solution of decachloro-*m*-carborane ($k = 0.9933$) in 50% alcohol, the pH-value

TABLE 5

VOLUMETRIC TITRATION OF HALOCARBORANES

No.	Compound	Mol. wt.	Weight (g)	Equiv. of KOH	KOH (ml)	
					A[a]	B[b]
1	$B_{10}Cl_{10}C_2H_2$	488.8	0.9990	0.09922	19.5	20.6
			1.0010	0.09922	19.8	20.6
2	$B_{10}Br_2Cl_8C_2H_2$	577.7	1.2097	0.10458	19.34	19.9
			1.1469	0.10458	18.37	18.9

[a] Amount of KOH required for titrating of weighed sample. [b] Theoretical amount of KOH required for titration of one C–H group.

TABLE 6

pK_a VALUES OF HALOCARBORANES

No.	Compound	pK_a	Error[a]	No. of measurements
1	o-$B_{10}Cl_{10}C_2H_2$	6.89	0.008	4
2	o-$B_{10}Br_2Cl_8C_2H_2$	6.95	0.015	4
3	o-$B_{10}Cl_{10}C_2HMe$	6.90	0.001	10
4	m-$B_{10}Cl_{10}C_2H_2$	9.19		1

[a] Here and elsewhere the mean square error is indicated.

was 8.54. After 2.5 h this value had decreased to 3.18. Consequently, pH measurements were made immediately after mixing KOH and decachloro-*m*-carborane solutions (*cf.* Table 6).

The value of $pK_a=9.19$ obtained, approximated to the mean of four values ($pK_a=9.08\pm0.03$) calculated using a point corresponding to 50% neutralization in the potentiometric titration curve of decachloro-*m*-carborane. The measurements were performed using "Radiometer", type SBR-2 (SBU-1) TTT-1c titrator. 15 ml of a 0.002 *M* solution of decachloro-*m*-carborane in 50% alcohol was titrated with aqueous 0.1 *N* KOH at room temperature; the titration required not less than 0.4 ml of KOH.

Determination of active hydrogen by the method of Tzerevitinov

A two- or three-fold excess of Grignard reagent (CH_3MgI) in dibutyl ether was added dropwise to the weighed sample (0.001–0.002 mole) in an argon atmosphere. The mixture was heated to complete the reaction and after the temperature had been adjusted the volume of methane was measured. o-$B_{10}Cl_{10}C_2H_2$, mol. wt. 488.8; 0.3615 g evolved 31.5 ml, calcd. 33.4 ml; 0.8031 g evolved 71.8 ml, calcd. 73.6 ml. o-$B_{10}Br_2Cl_8C_2H_2$, mol. wt. 577.7; 0.8674 g evolved 68 ml, calcd. 67.2 ml; 0.8142 g evolved 63.8 ml, calcd. 63.3 ml. m-$B_{10}Cl_{10}C_2H_2$, mol. wt. 488.8; 0.3091 g evolved 26.3 ml, calcd. 27 ml (the gas volumes are reduced values).

Triethyl- and trimethyl-ammoniumhalocarboranes

Benzene solutions of equimolar amounts of trialkylamine and halocarborane (cooled to 5°) gave a suspension which on further cooling with ice-water gradually precipitated. The solid was filtered off and washed with cold benzene. All the trialkylammoniumhalocarboranes prepared, reverted to the initial halocarboranes on dissolving the -onium salts in alcohol and acidifying with hydrochloric acid. The precipitate of halocarborane was filtered off, dried and recrystallized and identified by melting point and IR spectra.

Adducts of halocarboranes with dimethylformamide and dimethylsulfoxide were prepared by several methods.

Decachloro-o-carborane and Me_2SO. (*a*) 1.95 g (0.004 mole) of decachloro-*o*-carborane was dissolved in the minimum amount of Me_2SO and after 5–10 min the adduct, $B_{10}Cl_{10}C_2H_2Me_2SO$ (2.13 g, 94% theory), was precipitated by water. (*b*) 1.95 g (0.004 mole) of decachloro-*o*-carborane was dissolved in the minimum amount of Me_2SO and the mixture allowed to stand for a month at room temperature. The precipitated adduct was filtered off. 2.02 g (89% theory) of product was obtained. (*c*) 1.95 g (0.004 mole) of decachloro-*o*-carborane was dissolved in 10 ml of CH_2Ci_2 and 0.32 g of Me_2SO in 5 ml of CH_2Cl_2 was added. The reaction mixture warmed up appreciably and the solid gradually precipitated; 2.05 g (90% theory).

The initial halocarboranes were recovered from the Me_2SO or Me_2NCHO adducts either by two–three-fold recrystallization from aqueous alcohol or by dissolving the adduct in dilute alkali and acidifying with hydrochloric acid. The halocarboranes were identified by melting points and IR spectra.

Dodecachloro-o-carborane. To 1.95 g (0.004 mole) of decachloro-*o*-carborane dissolved in boiling carbon tetrachloride was added a solution of 0.3 g (0.004 mole) of NEt_3 in CCl_4. After 15 min, gaseous chlorine was passed through the refluxing mixture. After 1.5 h, the mixture was cooled and triethylamine hydrochloride filtered off. The filtrate was washed with water, dried with calcined $MgSO_4$ and evaporated. 1.45 g of dodecachloro-*o*-carborane was obtained (65% theory), m.p. 422–424° (dec.) (CCl_4). (Found: C, 4.37; B, 19.51; Cl, 76.46. $C_2B_{10}Cl_2$ calcd.: mol. wt. 557.7; C, 4.31; B, 19.40; Cl, 76.29%.)

1,2-*Dibromodecachloro-o-carborane* was prepared analogously to dodecachloro-*o*-carborane in 69% yield, m.p. 341–344 (dec.) (CCl_4). (Found: C, 3.76; B, 16.92; hal., 79.73. $B_{10}Cl_{10}C_2Br_2$ calcd.: mol. wt. 646.6; C, 3.71; B, 16.73; hal., 79.55%.)

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REFERENCES

1 H. SCHROEDER, T. L. HEYING AND G. R. REINER, *Inorg. Chem.*, 2 (1963) 1092.
2 L. I. ZAKHARKIN, V. I. STANKO AND A. I. KLIMOVA, *Izv. Akad. Nauk SSSR Ser. Khim.*, (1964) 771.
3 L. I. ZAKHARKIN, V. I. STANKO AND A. I. KLIMOVA, *Izv. Akad. Nauk SSSR Ser. Khim.*, (1966) 1946.
4 H. SCHROEDER, G. R. REINER, R. P. ALEXANDER AND T. L. HEYING, *Inorg. Chem.*, 3 (1964) 1464.

5 H. Schroeder and G. D. Vickers, *Inorg. Chem.*, 2 (1963) 1317.
6 H. D. Smith, T. A. Knowles and H. Schroeder, *Inorg. Chem.*, 4 (1965) 107.
7 J. D. Roberts and J. A. Vancey, *J. Am. Chem. Soc.*, 73 (1951) 1011.
8 G. Schwarzenbach and E. Rudin, *Helv. Chim. Acta*, 22 (1939) 360.
9 R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, 1 (1964) 1.
10 L. A. Leites, L. E. Vinogradova, V. N. Kalinin and L. I. Zakharkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, to be published.