Rearrangements of Icosahedral Monohalo-*m*-carboranes

Sir:

Polyhedral rearrangements of 9-bromo-*o*-carborane at 395–425° yield[1] all possible *ortho* and *meta* isomers, but yield no transformations of the *meta* isomers which are produced. Production of *p*-carborane[2] from *m*-carborane at 500–620° raises questions concerning the mechanisms of further transformations and the equilibrium distributions of products at these higher temperatures. We report here the results of rearrangements of 9-chloro-*m*-, 2-chloro-*m*-, 4-chloro-*m*-, 5-chloro-*m*-, chloro-*p*-, fluoro-*p*-2-fluoro-*m*-, and 4-fluoro-*m*-carboranes at 560–570°.

Starting from 9-chloro-*m*-carborane obtained by electrophilic chlorination,[3] which should yield 9-Cl substitution,[4] all other *meta* isomers and the *para* isomer were obtained after rearrangement and separation by preparative vpc methods. Identification was made by correspondence with the products in the earlier study, from which only the *para* isomer was absent. Estimates of dipole moments, based upon values for known compounds,[5] aided these identifications.

Table I. Distributions of Products from Substituted Carboranes A–F

	Cl-*p*	2-Cl-*m*	4-Cl-*m*	5-Cl-*m*	9-Cl-*m*
		A. 9-Cl-*m*			
1 hr	2	3	16	0	79
5 hr	8	15	40	5	31
36 hr	48	9	19	16	8
		B. 2-Cl-*m*			
1 hr	4	40	51	2	3
5 hr	16	16	42	8	17
55 hr	48	9	19	16	8
		C. 4-Cl-*m*			
1 hr	4	23	58	4	12
5 hr	16	16	42	10	18
48 hr	46	8	21	17	8
		D. 5-Cl-*m*			
5 hr	24	6	14	52	5
55 hr	48	8	19	18	8
		E. Cl-*p*			
5 hr	79	4	6	9	2
36 hr	48	8	18	17	9
		F. F-*p*			
49 hr	47	13	20	16	4

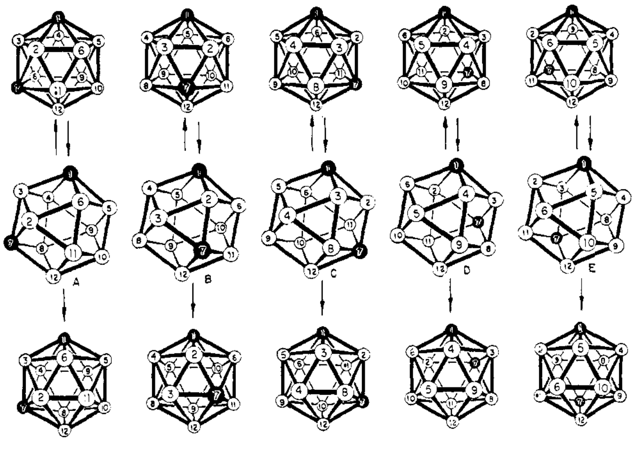

Figure 1. Cuboctahedral rearrangement processes. The five unique planar projections of the starting *m*-carborane (first line) lead to the five intermediates (second line) which open the icosahedron into the cuboctahedron in all possible ways. Triangle rotations, permitted only in the cuboctahedral intermediate, appear from the experiments to be favored if there is a halogen (Cl) attached to a B_2C triangle. Products in the last line are those produced if no triangle rotations occur, but pathway D leading to an *o*-carborane is not observed in the high-temperature range of 520–620°. Carbon atoms 1 and 7 are darkened.

Equilibrium distributions (Table I) are the same for all five starting monochlorocarboranes, and are nonstatistical in the sense that the Cl-*p* product is in unexpectedly high yield, and the 5-Cl product is slightly favored among *meta* isomers which statistically are in ratios of 20, 40, 20, and 20% for 2-Cl, 4-Cl, 5-Cl, and 9-Cl products, respectively. Molecular orbital energies[6] are comparable for idealized *m*- and *p*-carboranes but $C^{\delta+}\cdots C^{\delta+}$ repulsions may be less in the *para* isomer than in the *meta* isomer. An interesting, probably electronic,[7] effect in the final equilibrium for fluoro-*p*-carborane is the apparent preference of F for the more positive 2 position and less preference for the most negative[6] 9 position, as compared with the corresponding Cl-substituted carboranes. This same equilibrium distribution was also found when either 2-fluoro-*m*- or 4-fluoro-*m*-carborane was used as a starting material.

Initial transformations within the first hour (Table I) are clearly primarily from 9-Cl-*m* to 4-Cl-*m*, from 2-Cl-*m* to 4-Cl-*m*, from 4-Cl-*m* to 2-Cl-*m* and half as much 9-Cl-*m*, from 5-Cl-*m* to Cl-*p* and a comparable total of 4-Cl-*m*, 2-Cl-*m*, and 9-Cl-*m*, and from Cl-*p* to all *meta* derivatives in about the final proportions at all stages. The last two transformations of Cl-*p* and 5-Cl-*m* are slower than a very rough steady state which exists among 2-Cl-*m*, 4-Cl-*m*, and 9-Cl-*m* isomers after a few hours. Of the several mechanisms summarized in Table II, the pure cuboctahedral transformation[8] accounts for initial gross aspects of the 2-Cl-*m*, 4-Cl-*m*, and 9-Cl-*m* distributions, but triangle rotations *in the cuboctahedral intermediate* are required in order to convert 5-chloro-*m*- and chloro-*p*-carboranes to their products. Rotation of those triangles having a B–Cl bond would permit, perhaps by collision mechanisms,

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(1) H. D. Kaesz, R. Bau, H. A. Beall, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **89**, 4218 (1967).

(2) S. Papetti and T. L. Heying, *ibid.*, **86**, 2295 (1964).

(3) L. I. Zakharkin and V. N. Kalinin, *Dokl. Akad. Nauk SSSR*, [3] **169**, 590 (1966).

(4) H. A. Beall and W. N. Lipscomb, *Inorg. Chem.*, **6**, 874 (1967).

(5) (a) A. W. Laubengayer and W. R. Rysz, *ibid.*, **4**, 1513 (1965); (b) R. Maruca, H. Schroeder, and A. W. Laubengayer, *ibid.*, **6**, 572 (1967).

(6) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2872 (1967).

(7) This electronegativity effect is much more pronounced in the rearrangement of 3-fluoro-*o*-carborane at 420°. In this case only 4-fluor-*o*-, 2-fluoro-*m*-, and 4-fluoro-*m*-carborane are produced. In contrast, all three other *ortho* and all four *meta* isomers are produced[1] in the 3-bromo-*o*-carborane rearrangement at 420°.

(8) (a) A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 729 (1962); (b) R. Hoffmann and W. N. Lipscomb, *Inorg. Chem.*, **2**, 231 (1963); (c) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin Co., New York, N. Y., 1963, p 191; (d) W. N. Lipscomb, *Science*, **153**, 373 (1966).

the observed interconversions among 5-chloro-*m*-, chloro-*p*-, and 4-chloro-*m*-carboranes. A distribution matrix based upon mechanism b (Table II) does reproduce the intermediate yields as well as the final yields, but we cannot be sure that this mechanism is unique and we comment that triangle rotations are required to be less frequent relative to cuboctahedral rearrangements than they are in the 9-Br-*o* rearrangement in order to avoid a quasi steady state among 4-Cl-*m*, 5-Cl-*m*, and 9-Cl-*m* isomers.

Table II. Predicted Initial Product Distributions for the Cuboctahedral (a), Cuboctahedral with Triangle Rotations (b), Pentagonal Pyramidal Rotation (c), and Triangle Rotation (d) Mechanisms

	Product				
	2-Cl-*m*	4-Cl-*m*	5-Cl-*m*	9-Cl-*m*	Cl-*p*
		Mechanism a			
From 2-Cl-*m*	0.75	0.25	0	0	0
4-Cl-*m*	0.125	0.75	0	0.125	0
5-Cl-*m*	0	0	1.0	0	0
9-Cl-*m*	0	0.25	0	0.75	0
Cl-*p*	0	0	0	0	1.0
		Mechanism b[a]			
From 2-Cl-*m*	0.744	0.254	0	0.002	0
4-Cl-*m*	0.116	0.713	0.028	0.116	0.027[b]
5-Cl-*m*	0	0.031	0.932	0.01	0.027[b]
9-Cl-*m*	0.002	0.252	0.01	0.737	0
Cl-*p*	0	0.01[b]	0.01[b]	0	0.98
		Mechanism c			
From 2-Cl-*m*	0.5	0.167	0	0	0.333
4-Cl-*m*	0.083	0.417	0.167	0	0.333
5-Cl-*m*	0	0.333	0.167	0.167	0.333
9-Cl-*m*	0	0	0.167	0.5	0.333
Cl-*p*	0.167	0.333	0.167	0.167	0.167
		Mechanism d			
From 2-Cl-*m*	0.625	0.25	0	0	0.125
4-Cl-*m*	0.125	0.5	0.125	0.125	0.125
5-Cl-*m*	0	0.25	0.5	0.125	0.125
9-Cl-*m*	0	0.25	0.125	0.5	0.125
Cl-*p*	0.111	0.222	0.111	0.111	0.444

[a] B_3 and B_2C triangle rotations assumed to be equally probable.
[b] Adjusted to fit only the experimental final ratio of *para* to the sum of 4-Cl-*m* and 5-Cl-*m* (48:36).

Other mechanisms based either upon mutual rotations of two pentagonal pyramids[9] (Table IIc) or rotation by 120° of a triangular face in the icosahedron[10] (Table IId) fail to give the trends shown in the data. Assuming equal probability for all mutual rotations, the major faults are predictions of equal rates of conversion of each *meta* isomer to the *para* isomer, random return rates from *para* to a statistical distribution of *meta* isomers, large 4-Cl-*m* to 5-Cl-*m* to 9-Cl-*m* interconversions, and lack of account of the initial distributions. In addition, the rotating pentagon mechanism does not provide for 4-Cl-*m* to 9-Cl-*m* interconversions. No reasonable restrictions or modifications of these mechanisms could be devised to reduce substantially the strong tendency toward randomization which is not in accord with the experimental results.

The bromo- and iodo-*m*-carboranes decompose in this temperature range,[11] but further studies with dichloro derivatives and evaluation of thermodynamic and kinetic quantities are in progress.

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[10] E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, Inc., New York, N. Y., 1968, p 70.

[11] In the above experiments decomposition products (almost exclusively polymeric) averaged about 25% of the total.

Polarized Infrared Spectroscopy of Molecules Oriented in a Nematic Liquid Crystal. Application to $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$[1]

Sir:

Recent work in our laboratory has demonstrated that polarizations of electronic absorption bands can be obtained by orienting the molecule of interest in a nematic liquid crystal host.[2] We now wish to report that this new technique is useful for measuring the polarizations of absorption bands in the infrared region. The present communication describes the application of the method to obtain the first polarization data for infrared bands of binuclear metal carbonyls.

The compounds studied were the decacarbonyldimetal(0) complexes of Mn and Re; $Mo(CO)_6$ was included for reference. Solutions were prepared by dissolving approximately 1 mg of solute in 100 mg of the nematic phase of *p*-(*p*′-ethoxybenzoxy)phenyl butyl carbonate. Infrared spectra were taken at room temperature with a Perkin-Elmer 225 grating spectrophotometer equipped with wire grid polarizing optics. The cells consisted of two barium fluoride plates held in a stainless steel body and separated by a 0.0025-cm Teflon spacer. Uniform orientation of the nematic phase was achieved by rubbing the BaF_2 plates in one direction before introducing the sample. As was shown earlier,[2] this procedure is sufficient to produce uniform alignment of the nematic molecules in the direction of rubbing.

Figure 1 shows the polarized spectra of the liquid crystal solvent; it is apparent that many of the bands are strongly polarized. In the region where terminal C≡O stretching frequencies occur (2200–1900 cm^{-1}), absorption by the nematic solvent is not very significant, amounting in our cell to an absorbance of 0.15 or less when the electric vector is parallel to the long-axis orientation of the liquid crystal molecules. Thus, it is convenient to use this particular liquid crystal to study the polarizations of C≡O stretching bands.

Figure 2 gives the polarized spectra for $Re_2(CO)_{10}$ in the region 2100–1900 cm^{-1}. The spectra show that the

[1] This research was supported by the National Science Foundation.

[2] G. P. Ceasar and H. B. Gray, *J. Am. Chem. Soc.*, **91**, 191 (1969).