(8) Houser, K. J.; Bartak, D. E.; Hawley, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 6033.
(9) Nelson, R. F.; Carpenter, A. K.; Seo, E. T. *J. Electrochem. Soc.* **1973**, *120*, 206.
(10) Alwair, K.; Grimshaw, J. *J. Chem. Soc., Perkin, Trans. 2* **1973**, 1811.
(11) Renaud, R. N. *Can. J. Chem.* **1974**, *52*, 376.
(12) Asirvatham, M. R.; Hawley, M. D. *J. Am. Chem. Soc.* **1975**, *97*, 5024.
(13) Grimshaw, J.; Trocha-Grimshaw, J. *J. Chem. Soc., Perkin Trans. 2* **1975**, 215.
(14) M'Halla, F.; Pinson, J.; Savéant, J. M. *J. Electroanal. Chem.* **1978**, *89*, 347.
(15) Gores, C. J.; Koeppe, C. E.; Bartak, D. E. *J. Org. Chem.* **1979**, *44*, 380.
(16) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.
(17) Pinson, J.; Savéant, J. M. *J. Chem. Soc., Chem. Commun.* **1974**, 933.
(18) Pinson, J.; Savéant, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 1506.
(19) Amatore, C.; Chaussard, J.; Pinson, J.; Savéant, J. M.; Thiebault, A. *J. Am. Chem. Soc.* **1979**, *101*, 6012.
(20) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; Savéant, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 3431.
(21) Amatore, C.; Pinson, J.; Savéant, J. M.; Thiebault, A. *J. Electroanal. Chem.*, in press.
(22) Hammerich, O., personal communication, 1979.
(23) Jensen, B. S.; Parker, V. D. *J. Am. Chem. Soc.* **1975**, *97*, 5211.
(24) Cockrell, J. R.; Murray, R. W. *J. Electrochem. Soc.* **1972**, *119*, 849.
(25) Alavarado de la Torre, R.; Sease, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 1687.
(26) Amatore, C.; M'Halla, F.; Savéant, J. M., in course of publication.
(27) For a general analysis of the DISP–ECE problem, i.e., the competition between homogeneous and heterogeneous electron transfer following a first electron transfer step and a succeeding chemical reaction, see: Amatore, C.; Savéant, J. M. *J. Electroanal. Chem.* **1979**, *102*, 21, and references cited therein.
(28) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; M'Halla, F.; Savéant, J. M. *J. Am. Chem. Soc.*, in press.
(29) Amatore, C.; Savéant, J. M., in course of publication.
(30) Ingold, K. U. In "Free Radicals," Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, p. 77.
(31) Russell G. A. In ref. 30, p. 312.
(32) Savéant, J. M.; Su Khac Binh. *Bull. Soc. Chim. Fr.* **1972**, 3549.
(33) Savéant, J. M.; Su Khac Binh. *Electrochim. Acta* **1975**, *20*, 21.

Electrolytic Reduction of 1,4-Dihalonorbornanes at Mercury Electrodes in Dimethylformamide. Evidence for [2.2.1]Propellane as an Intermediate

William F. Carroll, Jr., and Dennis G. Peters*

Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47405. *Received December 24, 1979*

Abstract: Low-temperature (−34 °C) electrolytic reduction of 1,4-dibromonorbornane at mercury cathodes in dimethylformamide containing tetraalkylammonium perchlorates yields norbornane, bis(1-norbornyl)mercury, and 1,1′-binorbornyl; reduction of 1,4-diiodonorbornane results in the same three products along with 1-iodonorbornane and other minor species. At potentials for which the mass balance is 100%, norbornane and bis(1-norbornyl)mercury account for 98% of the electrolysis products and the coulometric *n* value is precisely three. When tetramethylammonium perchlorate is utilized as the supporting electrolyte at −34 °C, there is a range of potentials over which a pronounced polarographic current minimum appears; this low-temperature minimum is attributed to adsorption upon the electrode of complex species consisting of tetramethylammonium cations and halide ions. Three key observations suggest that [2.2.1]propellane is an intermediate in the electrochemical reduction of the 1,4-dihalonorbornanes: (1) norbornane is derived from 1,4-dihalonorbornane via a three-electron process which does not involve 1-halonorbornane as intermediate; (2) bis(1-norbornyl)mercury is produced by electrolytic reduction of 1,4-dihalonorbornane but not by reduction of 1-halonorbornane; and (3) a species apparently obtained by two-electron reduction of 1,4-dihalonorbornanes is capable of undergoing oligomerization. A polarographic wave seemingly attributable to reduction of [2.2.1]propellane is observed.

Electrochemical preparation of a propellane was first accomplished by Rifi,[1] who obtained [3.2.1]propellane by reduction of 1,5-dibromobicyclo[3.2.1]octane at a mercury pool cathode in dimethylformamide containing tetra-*n*-butylammonium perchlorate. In subsequent work, Wiberg and his collaborators[2,3] have attempted to electrosynthesize both [2.2.2]propellane and [2.2.1]propellane; although these two elusive small-ring propellanes have been implicated as intermediates in both chemical and electrochemical reactions, neither compound has been isolated. Wiberg, Epling, and Jason[2] demonstrated the probable intermediacy of [2.2.2]propellane in the electrolytic reduction of 1,4-dibromobicyclo[2.2.2]octane at platinum in dimethylformamide containing tetraethylammonium bromide. After the electrolysis was completed, the catholyte was saturated with chlorine gas and a small amount of 1,4-dichlorobicyclo[2.2.2]octane was recovered, the latter product resulting from addition of chlorine across the propellane bond. Wiberg, Epling, and Jason commented that [2.2.2]propellane is thermally unstable and undergoes a ring-opening reaction to produce 1,4-dimethylenecyclohexane; this diene adds chlorine across both double bonds to yield the tetrachloride.

In an investigation by Wiberg, Bailey, and Jason,[3] the reduction of 1,4-dibromonorbornane at a platinum electrode in dimethylformamide containing tetraethylammonium perchlorate was found to give norbornane, 1,1′-binorbornyl, and a norbornyl adduct of dimethylformamide. Although electrolyses were conducted at −25 °C, the experimental conditions were quite harsh because approximately one half of the supporting electrolyte was reduced along with the dibromide.[4] According to the authors, two different mechanisms could account for the formation of 1,1′-binorbornyl and the norbornyl adduct of the solvent—either coupling of the appropriate radicals or addition of radicals or anions to [2.2.1]propellane—but it was not possible to distinguish between these pathways from the available evidence.

The [2.2.1]propellane has been prepared and trapped (though not isolated or characterized) in the chemical reaction reported by Wiberg, Pratt, and Bailey.[5] Addition of *tert*-butyllithium to 1,4-diiodonorbornane at −77 °C results in an assortment of products, all of which appear to arise from addition of a carbanion to the [2.2.1]propellane.

We have recently undertaken investigations[6-11] of the electrochemical reduction of a number of alkyl halides, uti-

0002-7863/80/1502-4127$01.00/0

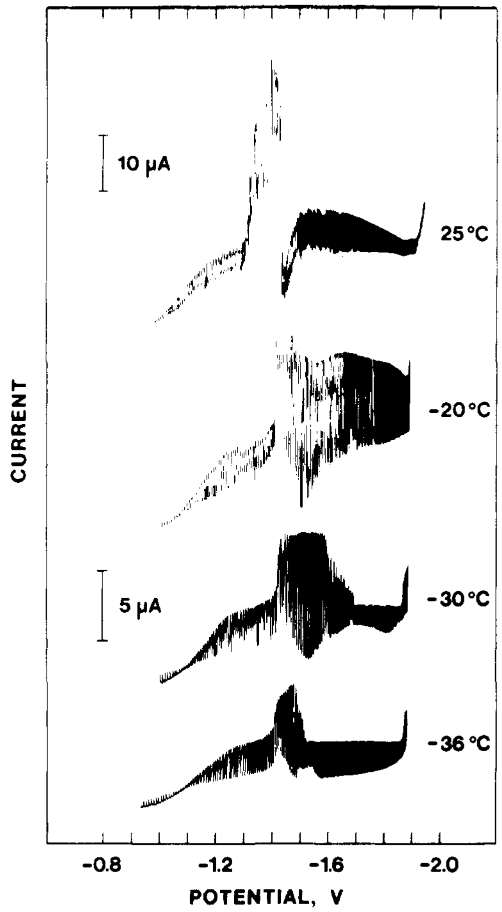


Figure 1. Polarograms for 0.0025 M 1,4-diiodonorbornane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate; 10-μA current scale applies to the upper polarogram and 5-μA current scale applies to the three low-temperature polarograms.

lizing dimethylformamide as solvent and tetraalkylammonium perchlorates as supporting electrolytes; mercury has been employed as the cathode material because it is convenient to use and because it is capable of trapping radicals generated on or near it.[6-13] We felt that study of the electrolytic reduction of 1,4-dihalonorbornanes would be more fruitful if carried out under milder conditions than those described by Wiberg and co-workers; and, if mercury cathodes were utilized, radicals such as those suspected by earlier investigators[3] might be trapped and identified. Accordingly, we report herein results of experiments that provide clearer evidence for the electrochemical generation and reduction of [2.2.1]propellane during the electrolysis of 1,4-dihalonorbornanes.

Experimental Section

Reagents. Dimethylformamide employed as solvent, tetramethylammonium perchlorate and tetra-*n*-butylammonium perchlorate used as supporting electrolytes, and pure nitrogen (99.98%) utilized for deoxygenation of solutions were all handled according to procedures outlined in an earlier paper.[8]

Preparation of 1,4-dibromonorbornane and 1,4-diiodonorbornane was accomplished by treatment of 1,4-dichloronorbornane with the aluminum foil-dihalomethane-bromine reagent of McKinley, Pincock, and Scott.[14] Synthesis of 1,4-dichloronorbornane involves addition of ethylene to hexachlorocyclopentadiene to give 1,2,3,4,7,7-hexachloronorborn-2-ene,[15] which can be hydrogenated over palladized charcoal to afford 1,4,7,7-tetrachloronorbornane;[16] reduction of the latter compound by diphenyltin dihydride results in 1,4-dichloronorbornane. Although yields of up to 63% were reported by Marchand and Weimar,[16] our best result from this procedure was the isolation of 1,4-dichloronorbornane in a yield of just 20%, despite rigorous purification and drying of all materials.

Instrumentation and Procedures. Equipment and electrolysis cells for polarography and controlled-potential coulometry are described elsewhere in more detail.[8,17] Controlled-potential electrolyses were performed with the aid of a Princeton Applied Research (PAR) Model 173 potentiostat-galvanostat equipped with a PAR Model 176 current-to-voltage converter capable of providing *iR* compensation; polarograms were recorded through the use of a PAR Model 175 Universal Programmer coupled to the potentiostat-galvanostat. All potentials are quoted with respect to a room-temperature reference electrode consisting of a saturated cadmium amalgam in contact with dimethylformamide saturated with both cadmium chloride and sodium chloride;[18,19] this electrode has a potential of −0.750 V vs. the aqueous saturated calomel electrode at 25 °C.

Complete procedures for the controlled-potential electrolyses and for the gas chromatographic determination of products are presented in a preceding publication.[8] Norbornane, 1-bromonorbornane, and 1-iodonorbornane were identified as electrolysis products by comparison of gas chromatographic retention times and mass spectra with those of authentic compounds.[20,21] Isolation and identification of bis(1-norbornyl)mercury are discussed in a previous report,[8] and the presence of 1,1′-binorbornyl among the products was confirmed by means of mass spectrometry.

Results and Discussion

Polarographic Behavior of 1,4-Diiodonorbornane and 1,4-Dibromonorbornane. Shown in Figure 1 are polarograms for 0.0025 M solutions of 1,4-diiodonorbornane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate at 25, −20, −30, and −36 °C. At room temperature, two waves are observed with diffusion currents in an approximate 2:1 ratio, the larger wave appearing at a more positive potential; however, a prominent current maximum[22] peaking at −1.40 V obscures the start of the second wave. As the temperature is lowered, the maximum diminishes and finally vanishes, the absolute magnitude of the polarographic current decreases, and a broad current minimum[23] appears on the plateau of the second wave. At a temperature of −36 °C, the minimum encompasses the unusually wide range of potentials from −1.52 to −1.87 V, and the diffusion current in this region is depressed to a level corresponding to that of the first polarographic wave.

Polarograms for 0.0025 M solutions of 1,4-dibromonorbornane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate at 25 and −36 °C are illustrated in Figure 2. Although the diffusion current for 1,4-dibromonorbornane at 25 °C and a potential of −1.7 V is comparable with the total diffusion current for 1,4-diiodonorbornane under the same conditions, there are significant differences in the behavior of the two compounds. Only a single polarographic wave with a much less pronounced current maximum is seen for 1,4-dibromonorbornane at room temperature. When the temperature is decreased to −36 °C, a vestige of the maximum at −1.46 V remains and the diffusion current for the dibromo species is depressed almost to zero between −1.60 and −1.80 V.

For the reduction of 1,4-diiodonorbornane in dimethylformamide containing 0.1 F tetra-*n*-butylammonium perchlorate, one observes at all temperatures a pair of somewhat poorly defined polarographic waves with diffusion currents in an ~2:1 ratio and upon which is superimposed a current maximum. As with other alkyl halides we have studied,[6-11] the polarographic maximum decreases in height and shifts toward more negative potentials as the temperature is lowered; moreover, the low-temperature current minimum, seen at relatively negative potentials only when tetramethylammonium cations are present, is absent. In dimethylformamide containing 0.1 F tetra-*n*-butylammonium perchlorate at 25 and −35 °C, the reduction of 1,4-dibromonorbornane gives a single polarographic wave.

Polarographic half-wave potentials for 1-halonorbornanes[8] and 1,4-dihalonorbornanes are listed in Table I. It is evident that the half-wave potential of the second wave for 1,4-diio-

Table I. Polarographic Half-Wave Potentials for 1-Iodonorbornane, 1,4-Diiodonorbornane, 1-Bromonorbornane, and 1,4-Dibromonorbornane in Dimethylformamide Containing Tetraalkylammonium Perchlorates

compd	$E_{1/2}$, V[a] 25 °C	−36 °C
A. 0.1 F Tetramethylammonium Perchlorate		
1-iodonorbornane	−1.22 ± 0.07[b]	−1.27
1,4-diiodonorbornane	−1.05, −1.38[b]	−1.12, −1.45
1-bromonorbornane	−1.67	−1.75[c]
1,4-dibromonorbornane	−1.35[b]	−1.40
B. 0.1 F Tetra-*n*-butylammonium Perchlorate		
1-iodonorbornane	−1.47	−1.58
1,4-diiodonorbornane	−1.18, −1.57[b]	−1.24, −1.63
1-bromonorbornane	−2.04	−2.20
1,4-dibromonorbornane	−1.55	−1.68

[a] All potentials are quoted with respect to the reference electrode described in the Experimental Section. Data for the 1-halonorbornanes are taken from ref 8. [b] A precise value for the half-wave potential is difficult to determine because of the presence of a polarographic maximum. [c] A value for the half-wave potential is difficult to determine because of the presence of a polarographic minimum; the actual half-wave potential may be somewhat more negative.

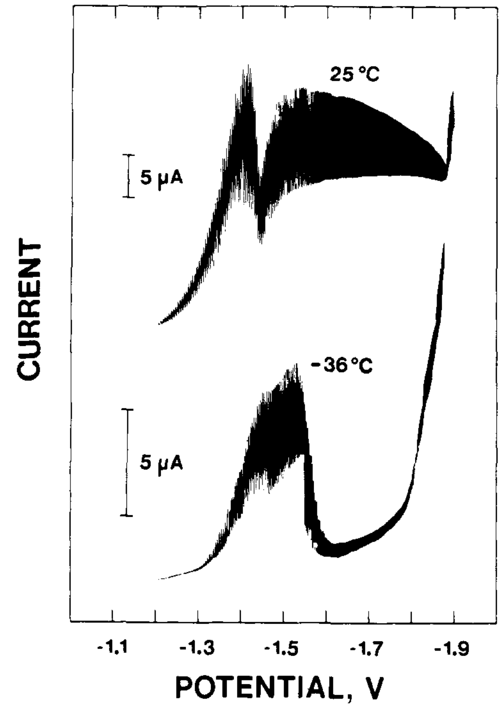


Figure 2. Polarograms for 0.0025 M 1,4-dibromonorbornane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate.

donorbornane does not coincide with the half-wave potential of the wave for 1-iodonorbornane; moreover, at room temperature the diffusion current of the second wave for the diiodide is roughly half that of the wave for the monoiodide.[8] This information suggests that 1-iodonorbornane is not the sole intermediate in the reduction of 1,4-diiodonorbornane. In addition, although 1-bromonorbornane and 1,4-dibromonorbornane both exhibit a single wave, the half-wave potential for the monobromide is at least 320 mV more negative than the half-wave potential for the dibromide; this fact indicates that, if 1-bromonorbornane is an intermediate in the reduction of 1,4-dibromonorbornane, the monobromide should be isolable because it is not electroactive at certain potentials.

Controlled-Potential Electrolyses of 1,4-Diiodonorbornane and 1,4-Dibromonorbornane. Results of controlled-potential electrolyses of 1,4-diiodonorbornane and 1,4-dibromonorbornane at mercury pool cathodes in dimethylformamide containing either 0.1 F tetramethylammonium perchlorate or tetra-*n*-butylammonium perchlorate at 25 and −34 °C are compiled in Tables II–VII; for each experiment, the concentration of starting material was 0.0025 M. It is obvious that the reduction of these compounds is highly sensitive to changes both in potential and temperature.

As revealed in Table II, electrolytic reduction of 1,4-diiodonorbornane in the presence of tetramethylammonium perchlorate at −34 °C results in a coulometric n value of ~1.6 at potentials (−1.0 to −1.2 V) corresponding to the rising portion of the first polarographic wave; 1-iodonorbornane is obtained in a yield ranging from 20 to 30%, along with small quantities of norbornane (≤5%) and 1,1′-binorbornyl (≤1%). As demonstrated previously,[8] 1-iodonorbornane is reduced to norbornane in a two-electron process, regardless of temperature and potential. Based upon the recovery of the monoiodide and the n value of <2, we surmise that the monoiodide is generated from the diiodide in a one-electron step at these potentials. Indeed it is highly improbable that the monoiodide could arise from two-electron reduction of the diiodide; Wiberg, Pratt, and Bailey[5] have demonstrated that the halo anion resulting from addition of two electrons to 1,4-diiodonorbornane preferentially undergoes intramolecular cyclization to yield [2.2.1]-propellane rather than protonation to give 1-iodonorbornane. On the other hand, because norbornane is an electrolysis product, some of the starting material must accept more than a single electron. For potentials (−1.3 and −1.4 V) on the plateau of the first polarographic wave for the diiodide, significant amounts of norbornane and bis(1-norbornyl)mercury are produced together with smaller yields of 1,1′-binorbornyl, and the n value lies between 2.2 and 2.5; because 1-iodonorbornane is easily reduced at potentials more negative than −1.3 V, it is only a minor product. Yields of norbornane and bis(1-norbornyl)mercury increase as the potential becomes more negative until ~50% of each compound is produced at a potential (−1.5 V) on the plateau of the second polarographic wave. Finally, reduction of 1,4-diiodonorbornane at a potential (−1.7 V) corresponding to the polarographic minimum gives results similar to those found in electrolyses done at potentials on the plateau of the first wave.

Table III shows that controlled-potential electrolyses of 1,4-dibromonorbornane at −34 °C with tetramethylammonium perchlorate as supporting electrolyte are characterized by n values from 2.2 to 2.9. Experiments performed at potentials (−1.4 and −1.5 V) on the rising portion of the polarographic wave yield only bis(1-norbornyl)mercury (70%) and norbornane (24%); no 1-bromonorbornane is found, even though it is not electroactive at these potentials and should be isolable. Electrolysis of a solution containing equal concentrations of 1-bromonorbornane and 1,4-dibromonorbornane at a potential causing reduction only of the latter results in recovery of 95% of the former; this observation, indicating no halogen transfer between the two compounds, establishes that norbornane is produced from 1,4-dibromonorbornane by a process not involving 1-bromonorbornane as intermediate.[24] At potentials (−1.6 to −1.8 V) encompassed by the low-temperature polarographic minimum, decreasing percentages of bis(1-norbornyl)mercury and norbornane are seen among the electrolysis products, but modest amounts (up to 10%) of 1,1′-binorbornyl do appear.

In several electrolyses of 1,4-diiodonorbornane and 1,4-dibromonorbornane at −34 °C in the presence of tetramethylammonium perchlorate (−1.5 V in Table II and −1.4, −1.5, and −1.6 V in Table III), the coulometric n value is virtually 3.0, the mass balance (total percentage of starting material incorporated into known products) is equal or close to 100%, and the only important products are norbornane and bis(1-norbornyl)mercury. Such observations indicate that norbor-

Table II. Coulometric Data and Product Distributions for Electrolytic Reduction at −34 °C of 1,4-Diiodonorbornane at Mercury in Dimethylformamide Containing 0.1 F Tetramethylammonium Perchlorate

			product distribution, %[a]			
potential, V	mass balance, %	*n* value	norbornane	1-iodonorbornane	1,1′-binorbornyl	bis(1-norbornyl)mercury
−1.00	31[b]	1.59	1	30		
−1.10	30[b]	1.60	4	26		
−1.20	26[b]	1.65	5	20	1	
−1.30	39	2.24	13	6	5	15
−1.40	41	2.47	18		6	17
−1.50	100	2.98	50		2	48
−1.60	75	2.83	35	3	3	34
−1.70[c]	40	2.27	20	1	6	13
−1.75[c]	27	2.22	16		7	4

[a] All yields are absolute percentages (determined with respect to an internal standard) of starting material incorporated into a given product; product yields and *n* values are based on the quantity of starting material actually consumed in an electrolysis. [b] Does not include 5–10% of unidentified high-molecular-weight products. [c] Potentials corresponding to the deepest region of the polarographic minimum.

Table III. Coulometric Data and Product Distributions for Electrolytic Reduction at −34 °C of 1,4-Dibromonorbornane at Mercury in Dimethylformamide

			product distribution, %[a]		
potential, V	mass balance, %	*n* value	norbornane	1,1′-binorbornyl	bis(1-norbornyl)mercury
		A. 0.1 F Tetramethylammonium Perchlorate[b]			
−1.4	94	2.86	24		70
−1.5	94	2.93	24		70
−1.6	92	2.90	43	1	48
−1.7[c]	66	2.75[c]	22	3	41
−1.8[c]	25	2.16[c]	7	10	8
		B. 0.1 F Tetra-*n*-butylammonium Perchlorate[d]			
−1.8	81	3.00	28	4	49
−1.9	67	2.73	24	9	34
−2.0	57	2.79	28	9	20
−2.1	78	2.90	60	8	10

[a] All yields are absolute percentages (determined with respect to an internal standard) of starting material incorporated into a given product; product yields and *n* values are based on the quantity of starting material actually consumed in an electrolysis. [b] No more than 1% of 1-bromonorbornane was recovered in any experiment done in the presence of tetramethylammonium perchlorate. [c] Potentials corresponding to the deepest region of the polarographic minimum; calculation of *n* value is complicated by erratic current–time trace. [d] No more than 3% 1-bromonorbornane and 5% tri-*n*-butylamine were recovered in any experiment done in the presence of tetra-*n*-butylammonium perchlorate.

Table IV. Coulometric Data and Product Distributions for Electrolytic Reduction at −34 °C of 1,4-Diiodonorbornane at Mercury in Dimethylformamide Containing 0.1 F Tetra-*n*-butylammonium Perchlorate

			product distribution, %[a]			
potential, V	mass balance, %	*n* value	norbornane	1-iodonorbornane	1,1′-binorbornyl	bis(1-norbornyl)mercury
−1.2	26[b]	1.61	3	22	1	
−1.3	26[b]	1.54	3	22	1	
−1.4	22[b]	1.65	4	11	2	5
−1.5	31[b]	2.09	8	7	3	13
−1.6	29	2.14	8	6	3	12
−1.7	39	2.56	13	1	4	21
−1.8	49	2.66	15	1	5	28
−1.9	68	2.86	33	1	3	31
−2.1	44	2.61	22	1	5	16

[a] All yields are absolute percentages (determined with respect to an internal standard) of starting material incorporated into a given product; product yields and *n* values are based on the quantity of starting material actually consumed in an electrolysis. [b] Does not include 5–10% of unidentified high-molecular-weight products.

nane and bis(1-norbornyl)mercury arise from transfer of three electrons to the starting materials. However, for most low-temperature electrolyses performed in the present investigation, compounds other than norbornane and bis(1-norbornyl)mercury are included among the roster of products and, moreover, the mass balance is substantially <100%; for these experiments, a simple calculation[25] suggests that any molecule of 1,4-dihalonorbornane not transformed into norbornane, bis(1-norbornyl)mercury, 1,1′-binorbornyl, or 1-iodonorbornane must undergo a two-electron reduction to yield a material which is not easily characterized. As discussed later, almost all of the unrecovered species appear to be oligomers derived from [2.2.1]propellane.

In general, the coulometric data and product distributions for reduction of the 1,4-dihalonorbornanes at −34 °C in solutions containing tetra-*n*-butylammonium perchlorate as supporting electrolyte closely parallel results discussed in the preceding paragraphs. For the diiodide (Table IV), the yield of monoiodide is highest at potentials corresponding to the rising portion of the first polarographic wave, whereas gener-

Table V. Coulometric Data and Product Distributions for Electrolytic Reduction at 25 °C of 1,4-Diiodonorbornane at Mercury in Dimethylformamide Containing 0.1 F Tetramethylammonium Perchlorate

			product distribution, %[a]			
potential, V	mass balance, %	*n* value	norbornane	1-iodonorbornane	1,1′-binorbornyl	bis(1-norbornyl)-mercury
−1.0	18	2.37	3	15		
−1.1	15	2.45	5	11	1	1
−1.2	20	2.18	13	1		7
−1.3	18	2.70	16			2
−1.4	54	3.24	39			15
−1.5	57	3.06	50			7
−1.6	70	3.46	68		3	1
−1.7	68	3.21	64		4	
−1.8	95	3.44	85		10	

[a] All yields are absolute percentages (determined with respect to an internal standard) of starting material incorporated into a given product; product yields and *n* values are based on the quantity of starting material actually consumed in an electrolysis.

Table VI. Coulometric Data and Product Distributions for Electrolytic Reduction at 25 °C of 1,4-Diiodonorbornane at Mercury in Dimethylformamide Containing 0.1 F Tetra-*n*-butylammonium Perchlorate

			product distribution, %[a]				
potential, V	mass balance, %	*n* value	norbornane	1-iodonorbornane	1,1′-binorbornyl	bis(1-norbornyl)-mercury	tri-*n*-butylamine
−1.2	23	1.77	3	17	2	1	1
−1.3	19	1.93	4	11	3	1	
−1.4	27	2.38	7	3	5	12	1
−1.5	54	2.90	22			32	8
−1.6	41	3.03	27			14	20
−1.7	60	3.05	33		1	26	NA[b]
−1.8	74	3.30	46		1	27	23
−1.9	73	3.07	60		1	12	31

[a] All yields are absolute percentages (determined with respect to an internal standard) of starting material incorporated into a given product; product yields and *n* values are based on the quantity of starting material actually consumed in an electrolysis. [b] Not available.

ation of norbornane and bis(1-norbornyl)mercury is greater at more negative potentials. For the dibromide (Table III), the production of norbornane is maximal at the most negative potentials and bis(1-norbornyl)mercury is formed in larger quantities at more positive potentials. For both of the 1,4-dihalonorbornanes, the yield of 1,1′-binorbornyl tends to increase as the potential becomes more negative.

Two minor products have been detected, though in yields of <2%, during low-temperature reductions conducted in the presence of either supporting electrolyte; first, 4,4′-diiodo-1,1′-binorbornyl is obtained from the electrolysis of 1,4-diiodonorbornane at the least negative potentials only and, second, a norbornyl adduct[26] of dimethylformamide has been seen in a number of experiments.

At 25 °C the pattern of reduction of 1,4-dihalonorbornanes is markedly different from, and somewhat less interesting than, the behavior of these compounds at low temperature. Presented in Tables V and VI are coulometric data and product distributions obtained from electrolyses of 1,4-diiodonorbornane in dimethylformamide containing tetramethylammonium perchlorate and tetra-*n*-butylammonium perchlorate, respectively. Except for potentials corresponding to the first polarographic wave, norbornane is the principal product and *n* values between 3.0 and 4.0 are recorded; small quantities of 1-iodonorbornane are generated upon reduction of the diiodide at the least negative potentials only, whereas 1,1′-binorbornyl is produced at the most negative potentials. Bis(1-norbornyl)mercury is recovered in yields of up to 32%, mainly when tetra-*n*-butylammonium perchlorate is employed as supporting electrolyte. Tri-*n*-butylamine, arising from the tetra-*n*-butylammonium cation via the Hofmann elimination, is formed in yields as high as 31% (based on the moles of starting material) at 25 °C; little, if any, of the amine is detected in electrolyses carried out at −34 °C.[27] Table VII contains the results of electrolyses of 1,4-dibromonorbornane at room temperature; the coulometric *n* value ranges from 3.15 to 3.83 and the products are norbornane (32–90%), bis(1-norbornyl)mercury (up to 25%), and 1-bromonorbornane (as much as 5%) along with tri-*n*-butylamine when tetra-*n*-butylammonium perchlorate is the supporting electrolyte.

Mechanism: Intermediacy of Propellane. With reference to the electrolytic behavior of 1,4-diiodonorbornane at −34 °C, there is a striking correlation between the magnitudes of the polarographic current and coulometric *n* value on one hand and the yields of norbornane and bis(1-norbornyl)mercury on the other hand. Figure 3, which represents graphically the data in Table II, illustrates the remarkably parallel variation of these quantities as a function of potential. On the basis of this information, we suggest that norbornane and bis(1-norbornyl)mercury are formed from 1,4-diiodonorbornane via a common intermediate. When coulometric data and product distributions for the electrolysis of 1,4-dibromonorbornane at −34 °C (Table III) are analyzed in a similar fashion, the yield of norbornane generally increases as the potential becomes more negative, whereas the amount of bis(1-norbornyl)mercury decreases steadily over the same range of potentials. Apparently, the mechanism by which norbornane and bis(1-norbornyl)mercury are produced is different for the two 1,4-dihalonorbornanes.

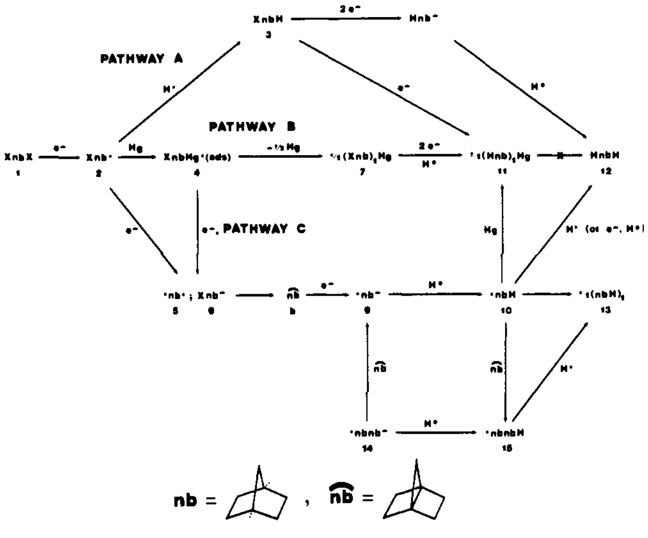
To explain how 1-iodonorbornane is generated from 1,4-diiodonorbornane at relatively positive potentials, we suggest that the 1-halonorbornane (**3**) arises via pathway A in Scheme I. As mentioned earlier, it seems logical that halo radical **2** rather than halo anion **6** is responsible for the formation of 1-iodonorbornane because Wiberg, Pratt, and Bailey[5] assert that cyclization of **6** is the preferred process at −77 °C, a reaction which should be no less facile at −34 °C. Indeed, if a higher temperature did favor protonation of **6** over internal cyclization, one would expect a marked increase in the yield of 1-iodonorbornane in room-temperature electrolyses com-

Table VII. Coulometric Data and Product Distributions for Electrolytic Reduction at 25 °C of 1,4-Dibromonorbornane at Mercury in Dimethylformamide

			product distribution, %[a]			
potential, V	mass balance, %	*n* value	norbornane	1-bromo-norbornane	bis(1-norbornyl)-mercury	tri-*n*-butylamine[b]
		A. 0.1 F Tetramethylammonium Perchlorate				
−1.3	58	3.64	32	2	24	
−1.4	77	3.42	60		17	
−1.5	82	3.53	73		9	
−1.6	94	3.62	94			
−1.7	84	3.83	84			
−1.8	90	3.74	90			
		B. 0.1 F Tetra-*n*-butylammonium Perchlorate				
−1.5	69	NA[c]	52		17	
−1.6	62	3.43	33	2	27	10
−1.7	66	3.28	45	4	17	20
−1.8	73	3.15	52	5	16	25
−1.9	75	3.33	68	4	3	24
−2.0	64	3.25	63	1		23

[a] All yields are absolute percentages (determined with respect to an internal standard) of starting material incorporated into a given product; product yields and *n* values are based on the quantity of starting material actually consumed in an electrolysis. [b] Does not apply to electrolyses in which tetramethylammonium perchlorate is used as supporting electrolyte. [c] Not available.

Scheme I



pared with those performed at −34 °C—but the opposite trend is observed.

Let us now recall three compelling pieces of experimental evidence: (a) norbornane is derived from 1,4-dihalonorbornane via a three-electron reduction which does not involve 1-halonorbornane as an intermediate; (b) large amounts of bis(1-norbornyl)mercury are produced by reduction of either 1,4-dihalonorbornane, but little or no diorganomercury compound is formed when the 1-halonorbornanes are reduced;[8] and (c) a species is obtained by two-electron reduction of 1,4-dihalonorbornanes that is capable of undergoing polymerization. Intermediacy of [2.2.1]propellane accounts for all these observations. Both the diradical (**5**)[28] and the halo anion (**6**)[5] can give rise to the propellane (**8**).[29] Propellane is known to react with anionic species at the bridgehead position;[5] linkage of two or more propellanes would generate oligomers (**14** and **15**) difficult to detect by means of gas chromatography.

To establish the existence of propellane-derived oligomers, an electrolysis of 1,4-diiodonorbornane was performed at a potential of −1.4 V in dimethylformamide containing 0.1 F tetramethylammonium perchlorate at 25 °C—conditions designed to maximize the yield of high-molecular-weight products. Subjecting the mixture of products to vacuum removed all low-molecular-weight species; the semisolid mass which remained showed infrared absorption bands characteristic of the norbornyl moiety and the carbonyl group of an amide, but no band attributable to the stretching mode of an alkene.[30] Mass spectrometry revealed the presence of the following molecular ions and fragments: *m/e* 355, $[H(C_7H_{10})_3CON(CH_3)_2]^+$; 261, $[H(C_7H_{10})_2CON(CH_3)_2]^+$; 233, $[H(C_7H_{10})_2N(CH_3)_2]^+$; and 189, $C_{14}H_{21}{}^+$. In addition, a species of *m/e* 167, $[H(C_7H_{10})CON(CH_3)_2]^+$, was detected in gas chromatographic-mass spectrometric experiments. In all these mass spectra, the base peak (*m/e* 95) corresponds to the 1-norbornyl system; species of mass 94 corresponding to [2.2.1]propellane are lost during the fragmentation process.

One-electron reduction of propellane (**8**) completes the alternate three-electron pathway to norbornane which does not involve 1-halonorbornane as intermediate.[31] Radical anion **9**, the product of this one-electron process, undergoes protonation to yield the 1-norbornyl radical (**10**). Once formed, the 1-norbornyl radical can gain a hydrogen atom from the solvent to give norbornane (**12**), can be adsorbed upon the mercury surface to eventually form bis(1-norbornyl)mercury (**11**), or can dimerize to produce 1,1′-binorbornyl (**13**). At −34 °C the two processes of adsorption of the 1-norbornyl radical upon the mercury pool and abstraction of a hydrogen atom from solvent by the 1-norbornyl radical appear to be competitive, because the yields of bis(1-norbornyl)mercury and norbornane are comparable. At room temperature, the preferred reaction is abstraction of a hydrogen atom by the 1-norbornyl radical or addition of another electron to the 1-norbornyl radical (followed by protonation), because the major electrolysis product is norbornane and the coulometric *n* value approaches 4.

At potentials corresponding to the low-temperature polarographic minimum, reduction of the propellane in the presence of tetramethylammonium perchlorate is blocked by adsorption onto the mercury cathode of complex species consisting of the tetramethylammonium cation and the halide ions released upon electrolysis of the 1,4-dihalonorbornanes.[23] If not reduced, the propellane reacts to form oligomers. We believe that this phenomenon explains why there is a close similarity between the coulometric *n* values and product distributions for electrolyses done at potentials corresponding to the plateau of the first polarographic wave and at potentials corresponding to the minimum for the reduction of 1,4-diiodonorbornane at −34 °C, because the second polarographic wave for 1,4-diiodonorbornane seems to be attributable to

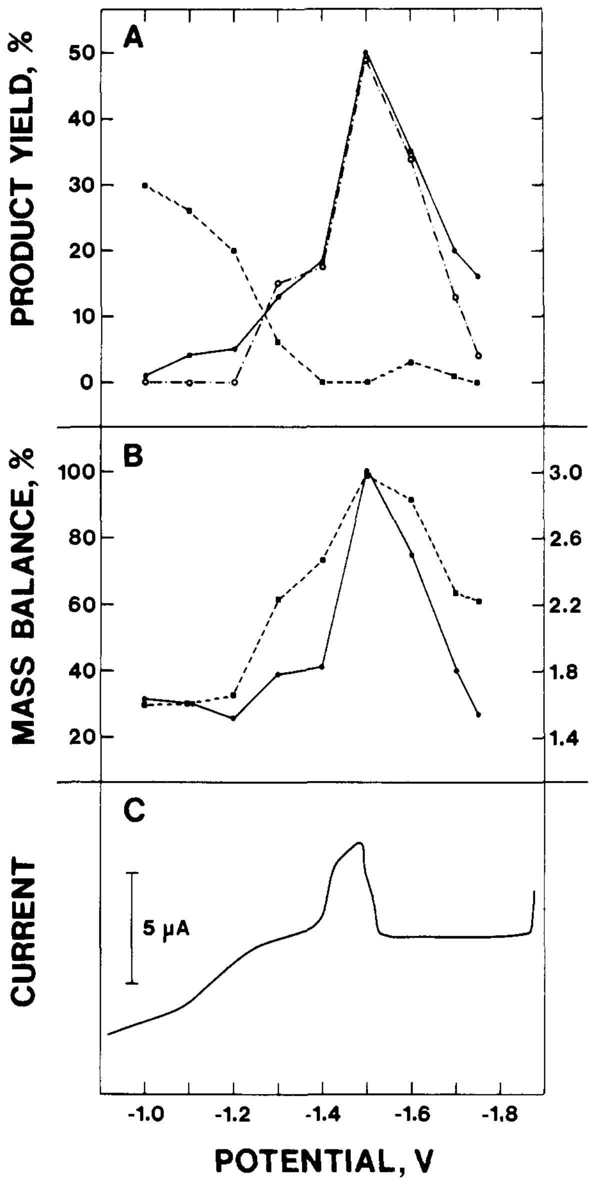


Figure 3. Characteristics of the electrolytic reduction of 1,4-diiodonorbornane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate at −34 °C: (A) absolute yields of norbornane (●), bis(1-norbornyl)mercury (○), and 1-iodonorbornane (■); (B) mass balance (—) and coulometric *n* value (- -); (C) smooth polarogram.

reduction of [2.2.1]propellane.

To rationalize differences in product distributions between the dibromide and diiodide as a function of potential, we must consider production of bis(1-norbornyl)mercury (**11**) via halo radical **2**. Webb, Mann, and Walborsky[12] have outlined a mechanism for the formation of dialkylmercury compounds involving adsorption of alkyl radicals upon the mercury cathode; combination of two adsorbed alkylmercury radicals and subsequent elimination of an atom of mercury result in the dialkylmercury species. This process is made possible by the presence of the electrode which stabilizes alkylmercury radicals.[32] Adsorption of **2** upon the electrode surface yields haloalkylmercury radical **4**, and reduction of **4** should be feasible[33] although the potential at which this reaction can occur may be highly dependent upon the identity of the halide; the 4-iodonorbornylmercury radical would be expected to be more easily reducible than the corresponding 4-bromonorbornylmercury radical by analogy to the pattern of reduction of simple alkyl monohalides.

Based on experimental data, it appears that competition exists between pathway B and pathway C in Scheme I, the rates of reactions in these pathways changing as a function of potential. For the reduction of 1,4-dibromonorbornane at the least negative potentials, pathway B contributes significantly to the formation of bis(1-norbornyl)mercury; pathway C predominates at more negative potentials because the 4-bromonorbornylmercury radical (**4**) may be reduced. On the other hand, pathway C is preferred over pathway B at all potentials during the reduction of 1,4-diiodonorbornane.

Although no bis(4-halo-1-norbornyl)mercury (**7**) has been recovered in the present investigation, it is conceivable that reduction of this species is easily accomplished. Casanova and Rogers[34] report that no bis(bromoalkyl)mercury compound results from the three-electron reduction of 1,ω-dibromoalkanes to dialkylmercury species; in addition, **7** may be particularly easy to reduce in view of the through-space interaction between the C_1 and C_4 sites.[35]

To date, efforts to isolate the propellane have been unsuccessful. Ultrasonic stirring of the solution in the electrolytic cell, coupled with continuous and rapid bubbling of nitrogen through the reaction mixture, failed to remove the propellane. After each attempt, however, polymer was recovered from the solution. Apparently, anions or radicals react with the propellane before it can escape from the diffusion layer at the electrode surface.

Acknowledgments. Appreciation is expressed to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We thank Daniel M. La Perriere and Brian C. Willett of Indiana University as well as William E. Pratt of Yale University for helpful suggestions.

References and Notes

(1) Rifi, M. R. *Collect. Czech. Chem. Commun.* **1971**, *36*, 932-935.
(2) Wiberg, K. B.; Epling, G. A.; Jason, M. *J. Am. Chem. Soc.* **1974**, *96*, 912-913.
(3) Wiberg, K. B.; Bailey, W. F.; Jason, M. E. *J. Org. Chem.* **1976**, *41*, 2711-2714.
(4) Using data contained in the experimental section of ref 3, one can compute that electrolysis of 500 mL of dimethylformamide containing 2.5 mmol of 1,4-dibromonorbornane and 50 mmol of tetraethylammonium bromide involved passage of a minimum of 2520 C (corresponding to 26 mmol of electrons).
(5) Wiberg, K. B.; Pratt, W. E.; Bailey, W. F. *J. Am. Chem. Soc.* **1977**, *99*, 2297-2302.
(6) McNamee, G. M.; Willett, B. C.; La Perriere, D. M.; Peters, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 1831-1835.
(7) La Perriere, D. M.; Willett, B. C.; Carroll, W. F., Jr.; Torp, E. C.; Peters, D. G. *J. Am. Chem. Soc.* **1978**, *100*, 6293-6294.
(8) Carroll, W. F., Jr.; Peters, D. G. *J. Org. Chem.* **1978**, *43*, 4633-4637.
(9) Carroll, W. F., Jr.; Peters, D. G. *Tetrahedron Lett.* **1978**, 3543-3546.
(10) Willett, B. C.; Moore, W. M.; Salajegheh, A.; Peters, D. G. *J. Am. Chem. Soc.* **1979**, *101*, 1162-1167.
(11) La Perriere, D. M.; Carroll, W. F., Jr.; Willett, B. C.; Torp, E. C.; Peters, D. G. *J. Am. Chem. Soc.* **1979**, *101*, 7561-7568.
(12) Webb, J. L.; Mann, C. K.; Walborsky, H. M. *J. Am. Chem. Soc.* **1970**, *92*, 2042-2051.
(13) Wagenknecht, J. H. *J. Electroanal. Chem.* **1974**, *52*, 489-492.
(14) McKinley, J. W.; Pincock, R. E.; Scott, W. B. *J. Am. Chem. Soc.* **1973**, *95*, 2030-2032.
(15) Wilcox, C. F., Jr.; Zajacek, J. G. *J. Org. Chem.* **1964**, *29*, 2209-2211.
(16) Marchand, A. P.; Weimar, W. R., Jr. *J. Org. Chem.* **1969**, *34*, 1109-1112.
(17) Moore, W. M.; Peters, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 139-144.
(18) Marple, L. W. *Anal. Chem.* **1967**, *39*, 844-846.
(19) Hall, J. L.; Jennings, P. W. *Anal. Chem.* **1976**, *48*, 2026-2027.
(20) Wiberg, K. B.; Lowry, B. R. *J. Am. Chem. Soc.* **1963**, *85*, 3188-3193.
(21) Lansbury, P. T.; Pattison, V. A.; Sidler, J. D.; Bieber, J. B. *J. Am. Chem. Soc.* **1966**, *88*, 78-84.
(22) Polarographic current maxima have been observed for the reduction of a number of alkyl halides in dimethylformamide containing tetraalkylammonium salts; see ref 6, 8, 10, and 11. Although the nature of this phenomenon has not been fully elucidated, we believe that it is associated with reduction of adsorbed organomercury radicals.
(23) Carroll, W. F., Jr.; Peters, D. G. *J. Electrochem. Soc.*, submitted for publication. It appears that low-temperature current minima seen for the reduction of alkyl halides in dimethylformamide containing tetramethylammonium perchlorate are caused by adsorption onto the dropping mercury electrode of complex species consisting of $(CH_3)_4N^+$ and halide ion released upon reduction of the alkyl halide.
(24) In this experiment, the initial concentrations of 1-bromonorbornane and 1,4-dibromonorbornane were each 0.0025 M in dimethylformamide con-

taining 0.1 F tetramethylammonium perchlorate at −34 °C and the potential was −1.5 V. Only the 1-bromonorbornane that was initially added could have been recovered, because none is generated by reduction of the dibromide; actually, 95% of the monobromide was recovered, inasmuch as a small amount is reduced to norbornane because the foot of the reduction wave for the monobromide occurs at a potential close to −1.5 V. If 1-bromonorbornane were an intermediate in the formation of norbornane from 1,4-dibromonorbornane, the monobromide (HnbBr, where nb = norbornyl) would presumably arise from the reaction sequence BrnbBr + $e^- \rightarrow$ ·nbBr + Br^- and ·nbBr + H· → HnbBr. Then, one can propose that HnbBr + ·nbBr → Hnb· + BrnbBr will be followed by Hnb· + e^- + H^+ → HnbH. Taken together, these processes should, in the electrolysis of the dibromide with added monobromide, cause the yields of norbornane and *bis(1-norbornyl)mercury* to increase and *decrease*, respectively, compared with those in an electrolysis of the dibromide without added monobromide and, in addition, significantly <100% of the added monobromide should be recovered. However, these effects were not observed; so we rule out the intermediacy of the monobromide.

(25) If it is assumed that the 1,4-dihalonorbornane which cannot be accounted for undergoes an electron-transfer reaction having only a single *n* value, we can calculate this *n* from the relationship n = (tabulated overall n value) $- \{\Sigma[(n_i)$ (yield of i)/100$]\}$, where n_i is the number of electrons involved in forming product i from the starting material and where "yield of i" is the tabulated percentage yield of product i.

(26) In our study, mass spectra revealed that this norbornyl adduct of dimethylformamide has a molecular weight of 167, but we have not been able to distinguish between $HCON(CH_3)(CH_2C_7H_{11})$ and $C_7H_{11}CON(CH_3)_2$. In work by Wiberg, Bailey, and Jason,[3] a species reported to be the first of these two adducts was obtained, but NMR data included no resonance assignable to the formyl proton.

(27) For electrolyses performed in organic solvents containing salts of tetraalkylammonium cations [except $(CH_3)_4N^+$], Hofmann elimination has been taken as prima facie evidence for the presence of carbanions. However, hydroxide ion has been demonstrated to cause Hofmann elimination at room temperature in dimethylformamide containing tetraethylammonium bromide; see Reed, R. C. Ph.D. Thesis, Wesleyan University, Middletown, Conn., 1971. Hydroxide ion may be formed by abstraction of a proton from water (an impurity in the organic solvent) by any strong bases; these bases include fragmentation products of deprotonated dimethylformamide as well as carbanions themselves.

(28) Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972,** *94*, 779–786.

(29) Direct cyclization of species **2** cannot be ruled out; this reaction would yield propellane and an iodine atom. After reduction of this iodine atom to iodide, however, the *n* values and products for this process would be identical with those derived from cyclization of **6.** These two processes are indistinguishable.

(30) It is conceivable that 1,3-dimethylenecyclopentane, the product of a ring-cleavage reaction of [2.2.1]propellane (see ref 3) might be the source of the polymeric material, although this ring-opening is theoretically disallowed (see ref 28). Moreover, the absence of an alkene stretching band argues against this possibility in the present work.

(31) Electrochemical reduction of a propellane is unprecedented, although direct experimentation on the more reactive of such species is obviously difficult. Wilcox and Leung (Wilcox, C. F., Jr.; Leung, C. *J. Org. Chem.* **1968,** *33*, 877–880) reduced 1,4-dichloronorbornane with lithium metal and obtained only 1,4-dilithionorbornane and no 4-chloro-1-lithionorbornane. This reaction might involve reduction of the dichloride to propellane and reduction of propellane by lithium metal to achieve the dianion.

(32) Kashin, A. N.; Ershler, A. B.; Strelets, V. V.; Butin, K. P.; Beletskaya, I. P.; Reutov, O. A. *J. Organomet. Chem.* **1972,** *39*, 237–243.

(33) Brown, O. R.; Thirsk, H. R.; Thornton, B. *Electrochim. Acta* **1971,** *16*, 495–503.

(34) Casanova, J. P.; Rogers, H. R. *J. Am. Chem. Soc.* **1974,** *96*, 1942–1944.

(35) Wood, D. E.; Bailey, W. F.; Wiberg, K. B.; Pratt, W. E. *J. Am. Chem. Soc.* **1977,** *99*, 268–269.

Completion of Koerner's Proof That the Hydrogens of Benzene Are Homotopic. An Application of Group Theory

J. Michael McBride

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. *Received November 29, 1979*

Abstract: For more than a century Koerner's elegant proof of the equivalence of the hydrogens in benzene has been almost totally ignored. The logic of the last step in his argument is faulty, but reformulation of the problem in the language of permutation groups show that his evidence was sufficient for the proof. Definitions necessary for applying group theory to abstract chemical structure discussions are proposed, and the following statement is proven: If a group of equivalence permutations **P** is transitive on a set of p chemical locations, where p is a prime number greater than 2, and **P** includes an element which exchanges two chemical locations, the number of isomers involving disubstitution among these equivalent locations is at most $(p - 1)/2$. Analogous arguments may prove useful in discussing the structure of fluxional molecules.

Wilhelm Koerner is remembered in most organic chemistry textbooks because of his method for systematic identification of the relative positions of multiple substituents on the benzene nucleus. This method applies only if the six substituent sites of the carbon core are equivalent, and Ladenburg's paper of 1874 is most often cited for proof of this equivalence.[1] Koerner had published his own equivalence proof 5 years earlier, but in an Italian journal so obscure that then, as now, his contribution was ignored.[2] His proof required only three pages in a 45-page paper entitled "Facts to Serve in Determining Chemical Position in Aromatic Substances". The only subsequent mention of this proof seems to have been in some of Koerner's later papers, in his obituaries,[3] and in a 1917 German translation of the Italian paper.[4]

The Koerner proof is as logically elegant as van't Hoff's discussion of tetrahedral carbon or Fischer's proof of the configuration of glucose. In a way it is superior to these because, not being tied to a geometric model, the arguments are as applicable to a vibrating or fluxional molecule as to a rigid structure.

Given the neglect of Koerner's proof, it may not be surprising that no one has noted a fault in the last step of his argument, where he retreated from an abstract to a geometric model. Below we summarize Koerner's discussion and then show, by recasting it in the language of permutation groups, that the proof can be completed rigorously using the evidence he cited. This completion vindicates Koerner's intuition that his evidence constituted a proof of the equivalence of the hydrogens in benzene, and we hope that the group-theoretical approach used to reformulate his arguments may prove useful in discussing more subtle structural questions for which rigid models are inappropriate.

Koerner's Proof

Koerner published his proof in 1869, 5 years before the van't Hoff-Le Bel hypothesis of tetrahedral carbon. In the positivist view of many established chemists geometric models of molecules were not subject to experimental test and were thus both inappropriate and insidious.[5] Introducing his paper Koerner wrote "The dogma of the impossibility of determining the

0002-7863/80/1502-4134$01.00/0