Electrochemical Reduction of 1-Iodonorbornane and 1-Bromonorbornane at a Mercury Cathode in Dimethylformamide

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Polarograms for 1-iodonorbornane and 1-bromonorbornane in dimethylformamide containing either tetramethylammonium perchlorate or tetra-*n*-butylammonium perchlorate exhibit single irreversible waves corresponding to electrolytic cleavage of the carbon–halogen bond. Shifts in the half-wave potentials for 1-iodonorbornane and 1-iododecane with changes in the identity of the supporting electrolyte cation imply that the latter compound can achieve preferred orientation for electron transfer at the surface of the cathode. Large-scale controlled-potential electrolyses of 1-iodonorbornane and 1-bromonorbornane indicate that approximately two electrons are transferred per molecule of starting material; the principal product is norbornane, and little or no bis(1-norbornyl)mercury is formed. Comparison of the electrochemical behavior of 1-halonorbornanes and 1-halodecanes suggests that the 1-norbornyl radical intermediate has a tendency to be reduced electrolytically or to accept a hydrogen atom from the solvent, whereas the 1-decyl radical undergoes adsorption onto mercury to eventually yield didecylmercury.

In a previous paper,[1] the electrochemical behavior of 1-iododecane and 1-bromodecane at mercury cathodes in dimethylformamide containing tetramethylammonium perchlorate or tetra-*n*-butylammonium perchlorate was discussed. Polarograms for the reduction of 1-iododecane exhibit a single irreversible wave having a large maximum on the limiting-current plateau. On the other hand, the polarographic reduction of 1-bromodecane under similar conditions gives one wave without a current maximum. Large-scale electrolyses of 1-iododecane over a wide range of potentials indicate that the net process is the one-electron reduction of the carbon–halogen bond, but that the distribution of products is strongly dependent on potential. For potentials positive with respect to the polarographic maximum, a very high yield of didecylmercury is obtained; however, for potentials more negative than the polarographic maximum, the percentage of didecylmercury falls abruptly and the products are decane, 1-decene, 1-decanol, and telomers resulting from addition to 1-decene of radicals derived from the solvent. Controlled-potential electrolytic reduction of 1-bromodecane results in the uptake of one electron; the products are the same as those obtained from 1-iododecane at relatively negative potentials, except that no didecylmercury is formed.

To gain more insight into processes involved in the reduction of alkyl halides at mercury, we have undertaken an examination of the electrochemistry of both 1-iodonorbornane and 1-bromonorbornane in dimethylformamide containing either tetramethylammonium perchlorate or tetra-*n*-butylammonium perchlorate. This investigation was prompted in part by the facts that the 1-norbornyl radical, which is far less stable than any other tertiary radical, has approximately the same reactivity as a primary radical and that the 1-norbornyl anion has roughly the same stability as a primary carbanion.[2-6] Thus, it was of interest to compare the electrochemical behavior of decyl and norbornyl halides because of their differing stereochemistry. In addition, there have been only two previous reports dealing with the electrochemistry of 1-halonorbornanes. In evaluating the effect of the supporting electrolyte on the kinetics of electron transfer, Fry and Krieger[7] measured polarographic half-wave potentials for a number of alkyl halides, including 1-bromonorbornane, in dimethyl sulfoxide. Sease, Chang, and Groth,[8] in an earlier study, determined the half-wave potential for 1-bromonorbornane in dimethylformamide containing tetraethylammonium bromide. However, neither paper provides information about the products formed by electrolysis of 1-halonorbornanes, nor is the mechanism of reduction elucidated.

This communication presents results of polarographic and controlled-potential electrolytic studies of the reduction of 1-halonorbornanes at 25 °C and at temperatures as low as −36 °C. Regardless of potential or temperature, approximately two electrons are transferred to each molecule of starting material, the principal electrolysis product is norbornane, and little or no bis(1-norbornyl)mercury is formed. Polarographic half-wave potentials have been found to be sensitive to changes in temperature and the size of the supporting electrolyte cation. Comparison of the electrochemistry of 1-halonorbornanes with that of 1-halodecanes[1] provides a basis for speculation about the factors controlling the formation of diorganomercury compounds at the electrode surface. Moreover, because 1-halonorbornanes are possible intermediates upon reduction of 1,4-dihalonorbornanes,[9] knowledge of the electrochemical behavior of the former species is essential.

Experimental Section

Reagents. Dimethylformamide employed as solvent throughout this research was Fisher Spectranalyzed material; before use, it was distilled at a pressure of 5 torr from calcium hydride and was stored either in vacuo or under nitrogen at room temperature. Tetra-*n*-butylammonium perchlorate and tetramethylammonium perchlorate, both purchased from the G. Frederick Smith Chemical Co., were used without further purification as supporting electrolytes; these salts were stored over Drierite. Pure nitrogen (99.98%), passed through heated (800 °C) copper turnings to remove residual oxygen and through a column of 8 mesh Drierite to remove any water, was employed for deaeration of all solutions.

Published procedures were utilized for the preparation of 1-bromonorbornane[10] and 1-iodonorbornane.[2] These syntheses involve conversion of 1-chloronorbornane to 1-lithionorbornane by means of a lithium–halogen exchange followed by reaction of the organolithium compound with the appropriate elemental halogen. It is noteworthy that comparable, if not better, yields of 1-bromonorbornane were obtained when 1,2-dibromoethane in ether was used to brominate 1-lithionorbornane. Synthesis of 1-chloronorbornane was accomplished by treatment of 2,2-dichloronorbornane with aluminum trichloride in a solvent composed of a mixture of pentane isomers; the 2,2-dichloronorbornane was prepared from the reaction of norcamphor (bicyclo[2.2.1]heptan-2-one) with a solution of phosphorus trichloride and phosphorus pentachloride.[11]

Instrumentation and Procedures. The electrolysis cell and equipment for controlled-potential coulometry are described elsewhere.[1,12] However, several modifications were made in the design of the cell to decrease its volume and to permit its use for low-temperature studies. First, the working electrode compartment of the cell had a capacity of 40 mL, whereas only 10 mL of supporting electrolyte–solvent was needed to fill the auxiliary electrode compartment. Second, electrical contact to the mercury pool cathode was made by means of a platinum wire sealed into a probe inserted through a female standard-taper port in the side of the cell; the platinum contact was designed to stay below the surface of the mercury pool, even when the mercury–solution interface was rapidly stirred. Third, an alcohol

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thermometer, secured by a Teflon thermometer holder, was inserted into the working electrode compartment through another port, with the bulb of the thermometer positioned 1 cm above the surface of the mercury pool. Partial immersion of the cell into a xylene–liquid nitrogen bath contained in a styrofoam ice bucket allowed low-temperature experimentation; the temperature of the solution in the working electrode compartment was kept constant to within ±2 °C by periodic addition of liquid nitrogen to the bath.

Controlled-potential electrolyses were performed through the use of a Princeton Applied Research Model 173 potentiostat–galvanostat equipped with a Model 176 current-to-voltage converter capable of providing *iR* compensation; polarograms were recorded with the aid of a 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;[13,14] this electrode has a potential of −0.750 V vs. the aqueous saturated calomel electrode at 25 °C.

Each controlled-potential electrolysis was preceded by a blank electrolysis of supporting electrolyte–solvent at a potential 100 mV more positive than the potential needed to reduce the supporting electrolyte. Blank electrolyses were continued until the current decayed to 150 μA at 25 °C and to 50 μA at −34 °C; before and during these electrolyses, the supporting electrolyte–solvent was deoxygenated with bubbling nitrogen. At the conclusion of a blank electrolysis, known amounts of 1-halonorbornane and an electroinactive internal standard (phenylcyclohexane) were injected into the working electrode compartment, and an electrolysis was performed at the chosen potential until the current decayed to less than 5% of its initial value. However, no electrolysis was extended beyond a time limit of 2.5 h. Moreover, during the actual electrolysis, nitrogen was not bubbled through the solution; instead, a nitrogen blanket was maintained above the solution in the working electrode compartment. These two precautions were taken to minimize the loss of volatile norbornane, one of the electrolysis products.

After the electrolysis was finished, the solution in the working electrode compartment was transferred into a separatory funnel containing ice water. A 25:1 (v/v) mixture of diethyl ether and *n*-pentane was added to extract the electrolysis products along with the electroinactive internal standard (phenylcyclohexane) and any unreduced starting material; the resulting organic phase was washed repeatedly with ice water until all of the ether had been removed. Care was taken to ensure that no product escaped as vapor from the separatory funnel. Then the pentane extract was immediately analyzed by means of gas chromatography; 20 × 1/8 in. and 12 ft × 1/8 in. aluminum columns, each packed with 10% OV-101 on 80–100 mesh Gas Chrom P, and a 20 × 1/8 in. aluminum column and a 5 ft × 0.25 in. copper column, each packed with 10% Carbowax M on 80–100 mesh Chromosorb W, were used for the chromatographic measurements. Peak areas were determined with the aid of a Hewlett-Packard 3380S integrator. Gas chromatography–mass spectrometry was performed as discussed in an earlier paper.[1] A Varian 220-MHz spectrometer was utilized to record NMR spectra, and all chemical shifts are reported in parts per million downfield from tetramethylsilane.

Identification and Determination of Products. When gas chromatographic retention times and mass spectra for the electrolysis products were compared to such data for authentic samples of appropriate compounds, norbornane was identified as the principal species resulting from reduction of both 1-iodonorbornane and 1-bromonorbornane. Gas chromatographic response factors for norbornane vs. the electroinactive internal standard (phenylcyclohexane) were measured, and the areas of the gas chromatographic peaks for these two materials were accordingly corrected to calculate the absolute yield of norbornane. Identification and quantitation of tri-*n*-butylamine (formed from the Hofmann degradation of tetra-*n*-butylammonium perchlorate when the latter is employed as supporting electrolyte) as well as any unreduced 1-halonorbornane were accomplished in the same fashion.

Another electrolysis product, bis(1-norbornyl)mercury, was identified by comparison of its mass spectrum and gas chromatographic retention time with those of an authentic sample prepared by reduction of 1,4-diiodonorbornane at a mercury cathode in dimethylformamide containing tetra-*n*-butylammonium perchlorate as supporting electrolyte.[9] Bis(1-norbornyl)mercury gave the following spectral data after being obtained pure by means of preparative-scale gas chromatography: NMR (C_6H_6) δ 1.24 (m, 16 H), 1.59 (dd, 4 H), and 2.50 (broad s, 2 H). Mass spectra at 70 eV yielded the following results, with relative abundances reported in parentheses: *m/e* 393 (M^+, 1.16), 392 (M^+, 2.16), 391 (M^+, 1.72), 390 (M^+, 1.97), 389 (M^+, 1.29), 95 ($M^+ - C_7H_{11}Hg$, 100), 67 ($C_7H_{11}^+ - C_2H_4$, 31.1), and 41 ($C_5H_7^+ - C_2H_2$, 16.3). Anal. Calcd for $(C_7H_{11})_2Hg$: C, 43.01; H, 5.67. Found: C, 43.27; H, 5.83.

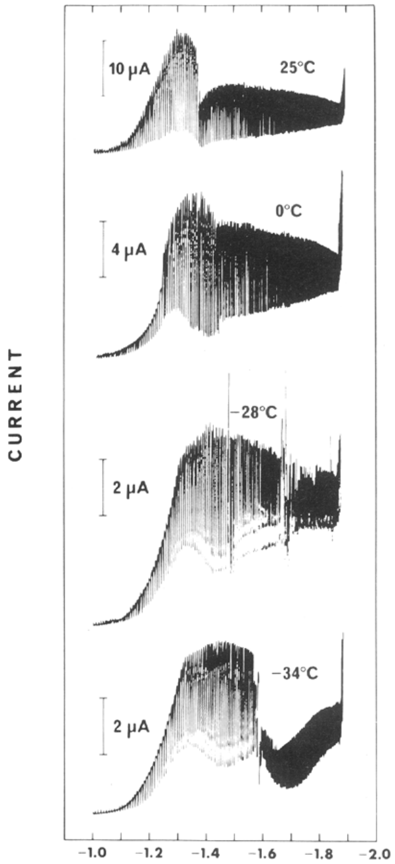


Figure 1. Effect of temperature on polarograms for reduction of 0.0025 M 1-iodonorbornane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate.

Because bis(1-norbornyl)mercury undergoes partial thermal decomposition on the injector of a gas chromatograph, the yield of this species derived from the electrolytic reduction of 1-bromonorbornane or 1-iodonorbornane was determined in a special way. Treatment of a pentane extract containing all of the electrolysis products with a saturated solution of iodine in glacial acetic acid quantitatively converts bis(1-norbornyl)mercury to 1-iodonorbornane, and the latter alkyl iodide can be determined as described above. Other electrolysis products are unreactive to the iodine–glacial acetic acid reagent. In studies of the electrolytic reduction of 1-iodonorbornane, the apparent yield of the alkyl iodide formed from decomposition of bis(1-norbornyl)mercury must be corrected for any unreduced alkyl iodide at the end of the electrolysis.

Results and Discussion

Polarographic Behavior of 1-Iodonorbornane and 1-Bromonorbornane. Polarograms for 0.0025 M solutions of 1-iodonorbornane in dimethylformamide containing 0.1 F tetramethylammonium perchlorate at 25, 0, −28, and −34 °C are shown in Figure 1. For the polarogram recorded at room temperature, there is a prominent maximum[15] peaking at −1.32 V which resembles that displayed by 1-iododecane under similar conditions.[1] Several things happen as the temperature is lowered. First, the absolute magnitude of the polarographic current decreases because the diffusion coefficient of 1-iodonorbornane becomes smaller. Second, the maximum on the rising portion of the polarographic wave recedes. Third, when the temperature reaches −29 °C, a current minimum suddenly appears; this minimum, clearly evident in the polarogram recorded at −34 °C, continues to deepen and widen as the temperature falls below −29 °C, reaching full development at −36 °C. Such a minimum has been observed

Table I. Polarographic Half-Wave Potentials for 1-Iododecane, 1-Iodonorbornane, 1-Bromodecane, and 1-Bromonorbornane in Dimethylformamide Containing Tetraalkylammonium Perchlorates

compd	temp, °C	$E_{1/2}$, V[a]
(a) 0.1 F tetramethylammonium perchlorate		
1-iododecane	25	−0.86
1-iodonorbornane	25	−1.22 ± 0.07[b]
1-iodonorbornane	−36	−1.27
1-bromodecane	25	−1.40
1-bromonorbornane	25	−1.67
1-bromonorbornane	−36	−1.75[c]
(b) 0.1 F tetra-*n*-butylammonium perchlorate		
1-iododecane	25	−1.35 ± 0.05[b]
1-iodonorbornane	25	−1.47
1-iodonorbornane	−36	−1.58
1-bromodecane	25	−1.81
1-bromonorbornane	25	−2.04
1-bromonorbornane	−36	−2.20

[a] All potentials are quoted with respect to the reference electrode described in the Experimental Section. [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.

in polarograms for the reduction of 1-iododecane, 1,4-diiodonorbornane, and 1,4-dibromonorbornane in dimethylformamide containing tetramethylammonium perchlorate at temperatures lower than −29 °C. We ascribe this low-temperature minimum to adsorption upon the mercury drop of complexes composed of tetramethylammonium and halide ions; this phenomenon will be explored more fully in a future paper.[16]

Polarograms for 1-iodonorbornane in dimethylformamide containing 0.1 F tetra-*n*-butylammonium perchlorate as supporting electrolyte at 25 and −36 °C exhibit neither the room-temperature maximum nor the low-temperature minimum, but a polarogram for 1-iododecane at room temperature recorded under the same conditions does show a maximum.[1] In dimethylformamide containing 0.1 F tetramethylammonium perchlorate or tetra-*n*-butylammonium perchlorate, a polarogram for 1-bromonorbornane at 25 °C consists of a single wave corresponding to irreversible reduction of the carbon–bromine bond. Polarograms for 1-bromonorbornane are unperturbed by the appearance of a maximum because 1-bromonorbornane is not electroactive in the region of potentials where maxima have been previously observed.[1] At temperatures below −33 °C, a polarogram for reduction of 1-bromonorbornane in the presence of 0.1 F tetramethylammonium perchlorate displays a minimum similar to that described for 1-iodonorbornane.[16]

A comparison of polarographic half-wave potentials for the reduction of 1-iodonorbornane, 1-iododecane, 1-bromonorbornane, and 1-bromodecane in dimethylformamide containing either tetramethylammonium perchlorate or tetra-*n*-butylammonium perchlorate at 25 and −36 °C is presented in Table I. Because the rising portion of the polarographic wave is partially masked by a current maximum, half-wave potentials at 25 °C for 1-iodonorbornane in the presence of tetramethylammonium perchlorate and for 1-iododecane in the presence of tetra-*n*-butylammonium perchlorate cannot be measured precisely. At a temperature of −36 °C, the polarographic wave for 1-bromonorbornane is not well defined due to the onset of reduction of the supporting electrolyte; hence, the half-wave potential is difficult to measure in the presence of either supporting electrolyte. Moreover, in solutions containing tetramethylammonium perchlorate, the aforementioned minimum further obscures a determination of the half-wave potential for 1-bromonorbornane. Nevertheless, it is evident from the data in Table I that 1-iododecane is easier to reduce than 1-iodonorbornane and that reduction of 1-bromodecane is more facile than reduction of 1-bromonorbornane.

Another feature of the results listed in Table I is that at a specified temperature the half-wave potential for each compound shifts toward a more negative value when the supporting electrolyte is changed from tetramethylammonium perchlorate to tetra-*n*-butylammonium perchlorate. Such a trend has been seen previously by Fry and Krieger,[7] who examined the polarographic behavior of a number of alkyl halides in dimethyl sulfoxide containing four different tetraalkylammonium salts. These workers demonstrated that an increase in the size of the supporting electrolyte cation causes a displacement of the half-wave potential to more negative values as well as a substantial decrease in the rate constant for heterogeneous electron transfer. Unfortunately, the unusually complicated polarographic behavior of the compounds in the present investigation prohibits the study of their electron-transfer kinetics by means of the procedure of Fry and Krieger.

It is interesting that at 25 °C the difference between the half-wave potentials for 1-iodonorbornane and 1-iododecane is much greater in the presence of tetramethylammonium perchlorate than for a solution containing tetra-*n*-butylammonium perchlorate. In seeking to explain this observation, we discount the possibility that in dimethylformamide there exist discrete complexes between the alkyl iodides and the tetraalkylammonium salts and that the relative stabilities of these complexes for each alkyl iodide differ disproportionately as a function of the identity of the supporting electrolyte. We believe the explanation lies in the fact that 1-iododecane undergoes especially facile reduction in the presence of tetramethylammonium perchlorate because the alkyl halide can approach the mercury cathode very closely. From a combination of polarographic and nuclear quadrupole resonance studies, Caldwell and Hacobian[17] concluded that, during the electrolytic reduction of phenyl iodides at mercury in water–ethanol mixtures containing tetramethylammonium iodide, the carbon–iodine bond is perpendicular to the electrode surface with the iodine atom being closer to the cathode. In a subsequent investigation of the reduction of alkyl iodides at lead electrodes in acetonitrile with tetraalkylammonium iodides as supporting electrolytes, Ulery[18] offered evidence to support the same preferential orientation of the carbon–halogen bond during electron transfer. It is eminently plausible to us that the particular ease of reduction of 1-iododecane, as well as methyl iodide and neopentyl iodide,[19] in dimethylformamide containing tetramethylammonium perchlorate might be attributable to a favorable orientation of the carbon–iodine bond. If the relatively small, adsorbable tetramethylammonium ion is replaced by the bulkier, adsorbable tetra-*n*-butylammonium cation,[20] or if substituents are introduced at the α carbon of the alkyl iodide (as is true for 1-iodonorbornane), the carbon–iodine bond cannot achieve its preferred orientation, the electron-transfer process is less facile, and the half-wave potential shifts to more negative values. Conceivably, such arguments underlie the aforementioned observations made by Fry and Krieger.[7]

Finally, it should be noted that the polarographic behavior of 1-bromonorbornane is especially sensitive to experimental conditions. As described earlier, polarographic waves corresponding to the reduction of 1-bromonorbornane are observed at room temperature in dimethylformamide containing either tetramethylammonium perchlorate or tetra-*n*-butylammonium perchlorate; Sease, Chang, and Groth[8] reported that

Table II. Coulometric Data and Product Distributions for Electrolytic Reduction of 0.0025 M 1-Iodonorbornane at Mercury in Dimethylformamide

			product distribution, %[a]		
electrolyte (temp, °C)	potential, V	*n* value	norbornane	bis(1-norbornyl)-mercury	tri-*n*-butylamine[b]
0.1 F tetramethylammonium perchlorate (25)	−1.2	1.72	83	5	
	−1.3	1.67	85	7	
	−1.4	1.96	83	3	
	−1.6	1.72	94	1	
	−1.8	1.85	97		
0.1 F tetramethylammonium perchlorate (−34)	−1.25	1.33	61	3	
	−1.4	1.88	93	3	
	−1.6	1.66	96	<1	
	−1.8	1.88	103	<1	
0.1 F tetra-*n*-butylammonium perchlorate (25)	−1.4	1.82	89	6	32
	−1.5	1.82	80	2	16
	−1.6	2.04	91		31
	−1.8	1.85	94		32
	−2.0	1.79	96		47
0.1 F tetra-*n*-butylammonium perchlorate (−34)	−1.5	1.50	83		2
	−1.7	1.75	99	1	1
	−1.9	1.75	94	1	12
	−2.0	1.91	96		<1

[a] All yields are absolute percentages determined with respect to an electroinactive internal standard (phenylcyclohexane) and based on the quantity of starting material consumed in a particular electrolysis. Coulometric *n* values are similarly based on the amount of starting material actually electrolyzed. [b] Does not apply to electrolyses in which tetramethylammonium perchlorate is used as supporting electrolyte.

Table III. Coulometric Data and Product Distributions for Electrolytic Reduction of 0.0025 M 1-Bromonorbornane at Mercury in Dimethylformamide

			product distribution, %[a]		
electrolyte (temp, °C)	potential, V	*n* value	norbornane	bis(1-norbornyl)-mercury	tri-*n*-butylamine[b]
0.1 F tetramethylammonium perchlorate (25)	−1.6	1.48	79	<1	
	−1.7	1.85	93	<1	
	−1.8	2.08	95	<1	
0.1 F tetramethylammonium perchlorate (−34)	−1.8	2.06	94		
0.1 F tetra-*n*-butylammonium perchlorate (25)	−1.9	1.95	102		32
	−2.0	2.02	94		36
	−2.1	2.27[c]	95		67[c]
0.1 F tetra-*n*-butylammonium perchlorate (−34)	−2.2	1.80	82		2

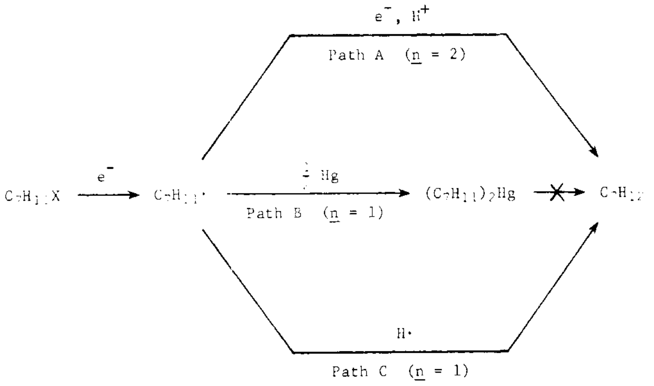
[a] All yields are absolute percentages determined with respect to an electroinactive internal standard (phenylcyclohexane) and based on the quantity of starting material consumed in a particular electrolysis. Coulometric *n* values are similarly based on the amount of starting material actually electrolyzed. [b] Does not apply to electrolyses in which tetramethylammonium perchlorate is used as supporting electrolyte. [c] Value is high, probably because of some electrolytic reduction of the supporting electrolyte.

1-bromonorbornane is reasonably well behaved in dimethylformamide with tetraethylammonium bromide. On the other hand, Fry and Krieger[7] obtained a polarographic wave for reduction of 1-bromonorbornane in a dimethyl sulfoxide–tetramethylammonium hexafluorophosphate medium, but no wave was seen when tetraethylammonium bromide or a tetraalkylammonium salt having larger alkyl groups was utilized as supporting electrolyte.

Controlled-Potential Electrolyses of 1-Iodonorbornane and 1-Bromonorbornane. Compiled in Tables II and III are coulometric data and product distributions obtained from controlled-potential electrolyses of 1-iodonorbornane and 1-bromonorbornane at mercury pool cathodes in dimethylformamide containing either tetramethylammonium perchlorate or tetra-*n*-butylammonium perchlorate at 25 and −34 °C. Coulometric *n* values for 1-iodonorbornane range from 1.7 to 2.0 at room temperature and from 1.3 to 1.9 at the lower temperature; *n* values for 1-bromonorbornane vary between 1.5 and 2.0. Norbornane is the principal product derived from the electrolytic reduction of both starting materials. In addition, small amounts of bis(1-norbornyl)mercury are recovered. For electrolyses performed in dimethylformamide containing tetra-*n*-butylammonium perchlorate, substantial yields of tri-*n*-butylamine are observed, especially in experiments done at room temperature; the latter product is presumably formed from the supporting electrolyte cation via Hofmann elimination, which indicates that carbanions are produced during an electrolysis. In general, the distribution of products listed in Tables II and III for the electrolyses at 25 °C tends to follow the pattern seen in a previous examination[1] of the electrolytic reduction of 1-iododecane and 1-bromodecane: (a) formation of bis(1-norbornyl)mercury from electrolysis of 1-bromonorbornane does not occur to any significant extent, and (b) although a very inefficient process, production of the diorganomercury compound by reduction of 1-iodonorbornane appears to be more important at potentials positive with respect to the polarographic maximum than at potentials more negative than the maximum.

To account for the formation of the various electrolysis products, we propose that mechanisms outlined in Scheme I are operative. Obviously, pathway A, which involves a two-electron reduction of the starting material accompanied by uptake of a proton, is the favored process. However, because of the appearance of small amounts of bis(1-norbornyl)mer-

Scheme I



$C_7H_{11} \equiv$ 1-norbornyl

cury and the observation of coulometric *n* values less than 2, we infer that pathways B and C contribute to the formation of products. When experiments are done in dimethylformamide containing tetra-*n*-butylammonium cation, the latter species serves as a proton donor, which explains why tri-*n*-butylamine (resulting from a Hofmann elimination) is found among the electrolysis products. Moreover, it is virtually inevitable that adventitious water as well as the solvent itself[21,22] competes with the supporting electrolyte as a source of hydrogen ions. Presumably, a radical produced by electrolytic reduction of starting material can accept a hydrogen atom from a molecule of solvent to yield norbornane or can interact with mercury to give bis(1-norbornyl)mercury according to the sequence of reactions described elsewhere.[1]

A comparison of 1-norbornyl and 1-decyl radicals indicates that, like their anions, they exhibit quite similar stability.[2-6] However, when formed by electrolysis of the appropriate alkyl iodide under equivalent electrochemical conditions (at potentials more positive than the polarographic maximum at room temperature), the 1-norbornyl radical is readily reduced to the anion which is protonated to yield norbornane, whereas the 1-decyl radical is adsorbed onto the mercury cathode, a process which leads to formation of didecylmercury via the combination–elimination reaction of a pair of adsorbed decylmercury radicals. It is reasonable to presume that there is competition among supporting electrolyte cations, solvent molecules, and alkyl radicals for available sites on the surface of the electrode; adsorption of a primary (1-decyl) radical should be favored over that of the bulkier 1-norbornyl radical purely on the basis of steric considerations, so the 1-norbornyl radical has a greater likelihood of accepting a hydrogen atom from a solvent molecule or of being reduced electrolytically. Succinctly stated, the rate of electron transfer to the alkyl radical is, on one hand, greater for the 1-norbornyl radical and, on the other hand, less for the 1-decyl radical than the rates of competing processes.

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Registry No.—1-Iododecane, 2050-77-3; 1-bromodecane, 112-29-8; norbornane, 279-23-2; 1-iodonorbornane, 930-80-3; 1-bromonorbornane, 13474-70-9; 2,2-dichloronorbornane, 19916-65-5; bis(1-norbornyl)mercury, 67773-54-0; tri-*n*-butylamine, 102-82-9.

References and Notes

(1) McNamee, G. M.; Willett, B. C.; La Perriere, D. M.; Peters, D. G. *J. Am. Chem. Soc.* **1977,** *99,* 1831–5.
(2) Lansbury, P. T.; Pattison, V. A.; Sidler, J. D.; Bieber, J. B. *J. Am. Chem. Soc.* **1966,** *88,* 78–84.
(3) Russell, G. A.; Janzen, E. G.; Strom, E. T. *J. Am. Chem. Soc.* **1964,** *86,* 1807–14.
(4) Wiberg, K. B.; Pratt, W. E.; Bailey, W. F. *J. Am. Chem. Soc.* **1977,** *99,* 2297–302.
(5) Lorand, J. P.; Chodroff, S. D.; Wallace, R. W. *J. Am. Chem. Soc.* **1968,** *90,* 5266–7.
(6) Fort, R. C., Jr.; Franklin, R. E. *J. Am. Chem. Soc.* **1968,** *90,* 5267–8.
(7) Fry, A. J.; Krieger, R. L. *J. Org. Chem.* **1976,** *41,* 54–7.
(8) Sease, J. W.; Chang, P.; Groth, J. L. *J. Am. Chem. Soc.* **1964,** *86,* 3154–5. Polarographic data for a number of mono- and dibromo bicyclic compounds are contained in the following reference: Závada, J.; Krupička, J.; Sicher, J. *Collect. Czech. Chem. Commun.* **1963,** *28,* 1664–74.
(9) Carroll, W. F., Jr.; Peters, D. G. *Tetrahedron Lett.* **1978,** 3543–6. "Abstracts of Papers", 174th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1977; American Chemical Society: Washington, D.C., 1977; ORGN 183.
(10) Wiberg, K. B.; Lowry, B. R. *J. Am. Chem. Soc.* **1963,** *85,* 3188–93.
(11) Wiberg, K. B.; Lowry, B. R.; Colby, T. H. *J. Am. Chem. Soc.* **1961,** *83,* 3998–4006.
(12) Moore, W. M.; Peters, D. G. *J. Am. Chem. Soc.* **1975,** *97,* 139–44.
(13) Marple, L. W. *Anal. Chem.* **1967,** *39,* 844–6.
(14) Hall, J. L.; Jennings, P. W. *Anal. Chem.* **1976,** *48,* 2026–7.
(15) This polarographic maximum does not exhibit the usual response to added suppressors; the reason for its appearance is still being investigated.
(16) Carroll, W. F., Jr.; La Perriere, D. M.; Torp, E. C.; Peters, D. G. "Abstracts of Papers", 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 1978; American Chemical Society: Washington, D.C., 1978; ANAL 56.
(17) Caldwell, R. A.; Hacobian, S. *Aust. J. Chem.* **1968,** *21,* 1403–13.
(18) Ulery, H. E. *J. Electrochem. Soc.* **1969,** *116,* 1201–5.
(19) Half-wave potentials measured in our laboratory are −0.80 V for methyl iodide and −0.94 V for neopentyl iodide in dimethylformamide containing 0.1 F tetramethylammonium perchlorate. Polarograms for both compounds display a maximum similar to that seen for either 1-iododecane or 1-iodonorbornane.
(20) Stokes radii for the tetramethylammonium and tetra-*n*-butylammonium cations are 2.04 and 4.71 Å, respectively: Robinson, R. A.; Stokes, R. H. "Electrolyte Solutions", 2nd ed.; Butterworths: London, 1965; p 125.
(21) Bánhidai, B.; Schöllkopf, U. *Angew. Chem., Int. Ed. Engl.* **1973,** *12,* 836–7.
(22) Campaigne, E.; Skowronski, G.; Forsch, R. A.; Beckman, J. C. *Synth. Commun.* **1976,** *6,* 387–97.